THE OXIDATION,

of

CAOUTCHOUC, GUTTA-PERCHA, AND BALATA.

----oOo--oOo--oOo----

John Todd,
The University,
GLASGOW.
April 1931.

- - - - - - - - - - -

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

PART I. Historical

A. Caoutchouc.

B. Gutta-Percha.

C. Balata.

PART II. Experimental.

PART III. Conclusion.

———————oOo———————

PART I. HISTORICAL.

A. Caoutchouc

---oOo---

Source.

In nature rubber occurs as a constituent of the latex of certain trees of tropical or sub-tropical origin, the most important source being the Hevea brasiliensis, a member of the botanical family Euphorbiaceae and a native of the Amazon valley. Latex is a white watery emulsion, contained in specialised microscopic tubes which are present in the cortex layer of the tree, a fact which shows that the latex is quite distinct from the tree sap which moves through the cambium and not the cortex layer. While the latex is to be found in all parts of the tree, only that contained in the trunk is utilised for commercial purposes. It is obtained by making a series of incisions in the bark and it exudes slowly from these to be collected in conveniently placed receptacles.

Rubber latex consists essentially of an emulsion of rubber in water. It contains however, in addition, other substances such as proteins, resin, sugars and inorganic materials, and the presence of protein is of especial importance because it acts as a protective colloid and prevents the coalescence of the rubber globules. Thus, the coagul-

ation of latex to give crude rubber depends on the removal of the protective film of protein and the neutralisation of the electric charges of the colloid particles. This result is achieved by heating the latex or by adding small quantities of coagulating agents such as mineral and organic acids and more especially acetic acid when a tough elastic mass of crude rubber is obtained.

Isolation of the Rubber Hydrocarbon.

Crude rubber, obtained by the coagulation of latex, contains, in addition to the hydrocarbon from which it receives its characteristic properties, resins, proteins, a small amount of sugars and some inorganic matter. Most of the carbohydrates are removed during the preliminary washing of the coagulated mass. Resins are removed by acetone extraction of the crepe, or product after passing the crude rubber through corrugated rollers revolving at unequal speeds, and the hydrocarbon obtained by dissolving the deresinised rubber in benzene, decanting the solution from insoluble material and precipitating the hydrocarbon by means of alcohol. The operation of dissolving in benzene and reprecipitating with alcohol is repeated several times. Harries(1) obtained by this method a fairly pure product which gave results of analyses agreeing quite well with the empirical formula C_5H_8.

Pummerer and Burkhard(2) have shown that the hydrocarbon

still contains small amounts of protein and sugars and a superior product, but still not always free from nitrogen, has been obtained by Pummerer and Koch(3) by fractional precipitation of a petroleum ether solution in acetone. Caspari(4) has obtained a very pure product by allowing the acetone-extracted rubber to stand in petroleum-ether or other similar solvent whereby the hydrocarbon diffuses slowly through the network of insoluble substances.

Pummerer and Pahl(5) have evolved a method for the purification of the rubber hydrocarbon by the direct use of preserved latex. The protein present is hydrolysed by treatment of the latex with sodium hydroxide solution after which creaming takes place when the mixture is allowed to stand. The lower alkaline layer is removed and the process repeated several times. The alkali remaining in the cream is removed by washing and by dialysis. The hydrocarbon is coagulated by addition of acetic acid and any remaining resins extracted with acetone before drying in a high vacuum. Analysis of the product obtained by this method agrees very closely with C_5H_8.

Physical Properties of Caoutchouc.

Caoutchouc, the pure rubber hydrocarbon, is tough and elastic, p. yellow and opague at the ordinary temperature but transparent above 20°, insoluble in alcohol and acetone

and soluble, after a preliminary swelling, in benzene, chloroform, carbon tetrachloride, carbon disulphide and similar solvents giving colloidal solutions. At 17°/4° the specific gravity of caoutchouc is 0.920.

It has long been recognised that caoutchouc contained two widely different constituents, and these can be separated by treatment of Pummerer and Pahl's product with absolute ether. In addition to the ether soluble constituent called "sol-rubber" or alpha-rubber, a difficultly soluble constituent is obtained and is named "gel-rubber" or beta-rubber. These two constituents are interconvertable; the gel-rubber becoming completely soluble in ether after thorough mastication, or breaking down on rollers, in an atmosphere of carbon dioxide while small amounts of gel-rubber, insoluble in ether, are obtained on evaporating an ether solution of sol-rubber. These observations seem to be evidence in favour of the view that rubber is a colloid system in which the disperse and continuous phases are modifications of the same hydrocarbon, differing only in their states of molecular complexity: Whitby(6) and Harries(7) considered the conversions mentioned above to be due to disaggregation and aggregation respectively; sol-rubber being disaggregated gel-rubber, and gel-rubber being

aggregated sol-rubber. Other workers thought that the two bodies were isomeric modifications of rubber, differing in the mode of arrangement of carbon and hydrogen atoms , a view which was unsupported by experimental evidence.

During a progressive purification of the hydrocarbon by fractional precipitation Pummerer and Koch(3) isolated crystals, giving an ultimate analysis corresponding with $(C_5H_8)x$. They exhibited very little elasticity and were much more easily oxidised in the air than ordinary non-crystalline material. When heated to 60° they became transparent and plastic and at 92° they melted completely. When examined crystallographically three crystalline types in six different formations were shown to be present. As these did not appear to be modifications of the same substances, they were ascribed to the presence of several chemically different substances.

No satisfactory determination of the molecular weight of caoutchouc has been made, on account of its nature as a colloid. Results obtained by the cryoscopic method vary greatly, some as high as 8,000-9,000 having been recorded. Hinrichsen and Kindscher(8) measured the depression of the freezing-point in a benzene solution of caoutchouc and resin, evaporated the solvent and weighed the residue. They then extracted the resin by means of

acetone and, after re-weighing, determined its molecular weight. They calculated the molecular weight of caoutchouc by difference and obtained the figure 3173. Pummerer, Nielsen, and Gündel(9) have used camphor as a solvent and obtained results of 1100 and 1600 employing concentrations of 1:4 and 1:10. Using menthol they obtained values of 1200-1600 at a concentration of 1:50 and 520 to 620 at a concentration of 1:100. From these results it would appear as if dilution had caused extensive depolymerisation. These lower values were obtained with products, purified in various ways, and with both sol- and gel-rubber.

Within recent years the study of caoutchouc by means of X-rays (10) (11) (12) (13) has received a good deal of attention. The diagram obtained with raw rubber is typical of an amorphous substance but, when it is stretched beyond 72% elongation, definite interference spots appear and these increase in intensity as the stretching is increased, showing a continual appearance of crystal grains. When the tension is released, the amorphous diagram is obtained again.

Products of the Destructive Distillation of Caoutchouc.

The earliest researches on caoutchouc were investigations on the products obtained from it by destructive distillation. As early as 1833 Barnard(14), by the thermal decomposition

of caoutchouc at 315°C., obtained an oily distillate which he termed caoutchoucine. When rectified, this liquid gave fractions of varying specific gravity, the lightest of which was .670. The following year Beale and Enderby(15) recorded a yield of 83⅓%, of an oil of specific gravity, .640 boiling below 38°C. The oil caoutchoucine was analysed by Dumas who found it was composed of carbon and hydrogen in the ratio C 88% H 12% . Himly(16), in 1835, obtained a 75% yield of an oil, from which he separated a portion of boiling-point 56-96°C and this gave, on fractionation, a volatile oil of specific gravity .654 and boiling-point 33-44°C, termed by him "Faradayin". Another fraction described by Himly gave a transparent oil of specific gravity .8423, boiling at 171°.5 which he called "caoutchine". From vapour density measurements and ultimate analysis he assigned to it the formula $C_{10}H_{16}$. In 1836, Gregory(17) obtained a highly rectified oil of sp. gr. .670 and b.p. 35°.5C, which gave, on treatment with sulphuric acid, an oil of b.p, 220° having the same composition as oil of turpentine.

Bouchardat(18), in 1837, made a more complete investigation of the products of destructive distillation. He isolated a hydrocarbon to which he gave the name "hevéène."

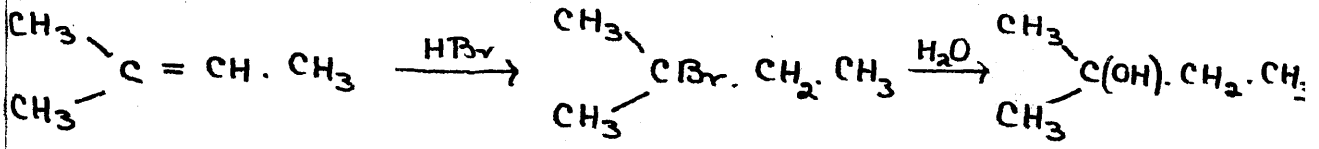
This was a transparent yellow oil of sp. gr. .921 and b.p. 252° which, on treatment with strong sulphuric acid, yielded a liquid of b.p. 182° considered by Bouchardat to be identical with the product obtained by the acid treatment of Gregory's light oil. He obtained also a transparent oil of sp. gr. .69 distilling at 63.7°.

It was in 1860 that Greville Williams,(19) took up the study of the destructive distillation of caoutchouc. He stopped the distillation before the hevéène fraction had passed over and, from the distillate, isolated two main fractions, one boiling at 37-44°C, and the other at 170-180°. From the first fraction he obtained a liquid of sp.gr. .6823 and b.p. 37-38°C. which he named "isoprene". Analysis and vapour density values indicated C_5H_8. The second fraction yielded a portion boiling at 170-173° identical with Himly's caoutchine of b.p.171°. The vapour density was double that of isoprene and it was thus isomeric with oil of turpentine.

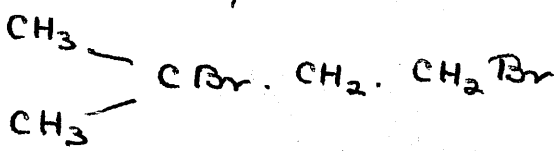
In 1885 Wallach (20) showed the identity of the tetrabromide of the caoutchine obtained by Himly, Bouchardat, and Williams with the tetrabromide of cinene, now called dipentene. He concluded that caoutchine and cinene were identical. Further evidence of the identity of caoutchine and dipentene was forthcoming from the work of Bouchardat

and Lafont(21) who, in 1886, obtained terpineol acetate, $C_{10}H_{16}O_2H_4O_2$, by the action of glacial acetic acid on cacutchine. When hydrolysed with hydrochloric acid, this substance gave cacutchine dihydrochloride and acetic acid When hydrolysed with alcoholic caustic potash it gave terpineol. On treatment of this with hydrochloric acid gas, the same dihydrochloride as above, $C_{10}H_{16}.2HCl$. was formed. Wallach proved the identity of this compound with dipentene hydrochloride.

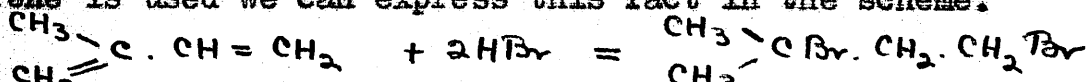
Previous to this, in 1882, Tilden(22) had studied the properties of isoprene obtained from sources other than rubber. For example, from turpentine oil, by passing it through a red-hot tube, he got a liquid, b.p. 37°, of vapour density corresponding to C_5H_8, and apparently identical with isoprene from rubber. From his observations he suggested the formula $\begin{matrix} CH_3 \\ CH_2 \end{matrix} > C.CH = CH_2$ i.e. β - methyl crotonylene. In 1897, Ipatieff and Wittorf(23) identified trimethyl ethylene in the isoprene fraction, 33-38°. They found that on treatment of this fraction with hydrobromic acid, there is formed a hydrobromide which gives dimethyl ethyl carbinol when treated with water and potassium carbonate. The formation of this compound from trimethyl ethylene is expressed as follows:-



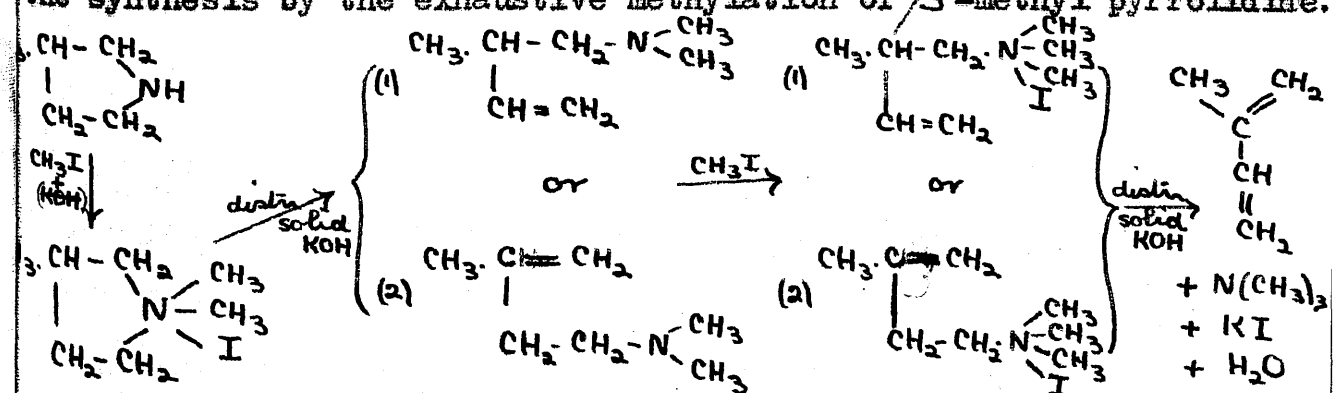
However, the main product of the action of hydrobromic acid on the isoprene fraction is β-dimethyl trimethylene bromide



identical with the bromide from dimethyl allene which, Gadziatzky (24) discovered, is formed when isoprene is heated with dilute alcoholic hydrochloric acid. If the Tilden formula for isoprene is used we can express this fact in the scheme.



Confirmation of the constitution of isoprene was given finally by Euler(25), in 1897, when he synthesised methyl crotonylene and showed it to be identical with isoprene. He achieved the synthesis by the exhaustive methylation of β-methyl pyrrolidine.



Harries(26), in 1902, distilled caoutchouc in a vacuum of 0.25mm. pressure and obtained as main fraction

an oil boiling at 220-260°C. with small amounts only of isoprene (1%) and dipentene. In 1922, Staudinger and Fritschi(27), employing a vacuum of 0.1-0.3mm. pressure and a final temperature of 350°C found that a resinous mass, amounting to about 36.5% of the original material and considered to be a polycyclo rubber, was left in the flask and that the distillate gave on fractionation 3.1% isoprene and 8.8% dipentene together with 4.4% of a $C_{15}H_{24}$ hydrocarbon containing two double bonds and two rings, possibly a derivative of hydronaphthalene, and 3.8% of a $C_{15}H_{24}$ hydrocarbon with three double bonds and two rings, and, finally, a $C_{25}H_{40}$ hydrocarbon with four double bonds and two rings. When the polycyclo rubber formed was decomposed at 350-400°C, neither isoprene nor dipentene were obtained.

More recently, Staudinger and Geiger(28) have distilled caoutchouc rapidly, at the ordinary pressure in an atmosphere of carbon dioxide, and obtained a 92.8% yield of volatile products, o.4% of this being liquid at -80°C. 2.6% had a b.p. 25.32°, 4.3% boiled at 32-35° and was the isoprene fraction, 23.8% was the dipentene fraction, 5.8% boiled at 50-70° at 12mm., and 25.9% above 180° at 12mm. When the distillation was carried out more slowly the amount of polycyclo rubber increased.

It is to be noticed that the yields of isoprene, which can give a rubber-like substance by polymerisation, are very small. This is probably due to the fact that, under the conditions necessary to produce decomposition of the rubber, isoprene does not polymerise to a rubber-like substance but gives dipentene and higher terpenes. Evidence in favour of the view that isoprene is the primary product of the destructive distillation of caoutchouc has been brought forward recently by Midgley and Henne(29) who have obtained unusually large yields (10%) of isoprene by very rapid distillation of large quantities of rubber.

Synthetic Rubbers.

About the same time as work was begun on the destructive distillation of caoutchouc, attention was directed to the repolymerisation of the distillate from such a process. In 1860, Williams(19) observed that some of his isoprene fraction, which had been kept for several months, had lost its fluidity and become "ozonised" and viscous. On careful distillation, a white spongy mass remained after the unchanged isoprene had distilled over. This residue he found to contain oxygen. Apparently, repolymerisation of the isoprene had occurred to some extent.

The next published work in this field was by Bouchardat

(30) who, in 1875, reported that he had obtained a viscous sticky mass by heating isoprene for some hours in a sealed tube at 280°. He distilled his product and got some isoprene together with a hydrocarbon, boiling at 170-185° and analysing for $C_{10}H_{16}$ and also higher boiling products. From a study of the two hydrochlorides obtained from his hydrocarbon b.p. 174°.5, he considered it to be identical with terpilene or dipentene. Four years later (31) he treated isoprene with concentrated aqueous hydrochloric acid at 0° and claimed to have prepared a synthetic caoutchouc. The elastic polymer which was formed was insoluble in alcohol, swelled before dissolving in ether and carbon disulphide, and gave the same heat decomposition products as caoutchouc.

In 1882, Tilden(22) observed that the isoprene which he had obtained by passing turpentine through a red-hot tube was polymerised to a caoutchouc-like substance by means of nitrosyl chloride or concentrated hydrochloric acid. Two years later (32) he polymerised isoprene by heating and obtained dipentene and a viscous polymeride which became tough and elastic on treatment with cold concentrated acid. In 1886, Wallach(33), who previously had confirmed the formation of dipentene by polymerisation of isoprene (20), observed that isoprene polymerised

to a tough caoutchouc-like mass on long exposure in a sealed tube to sunlight. In 1892, Tilden(34) noticed that some isoprene which had been standing for several years, had been converted into a substance which, in appearance and behaviour, was very similar to natural rubber. This spontaneous polymerisation of isoprene to rubber was confirmed, in 1894, by Weber(35) who then suggested that the rubber hydrocarbon might be called "polyprene".

The next observation of importance was that by Kondakow who, in 1900 and 1901 (36) (37), found that $\beta\gamma$-dimethyl-butadiene could be polymerised to a rubber-like product. Since then this work has been extended greatly and now we have many of these so-called methyl-rubbers, produced by polymerisation of homologues of isoprene. It has been shown that these synthetic products are not identical with natural rubber. For instance, Harries (38) has shown that the products obtained by hydrolysis of the ozonides of caoutchouc and dipropylene rubber are quite different.

Some of the above work has been repeated by Pond(39). He made vain attempts to obtain a polymerisation product by the action of hydrochloric acid on a sample of isoprene which had been frequently distilled. Harries(40), in 1913, suggested that the spontaneous polymerisation products

of Wallach(33) Tilden(34) and Weber(35) were not true caoutchoucs but were analoguous to the product obtained by Kondakow(37) from $\beta\gamma$-dimethyl-butadiene by the action of alcoholic caustic potash.

Constitution of Caoutchouc.

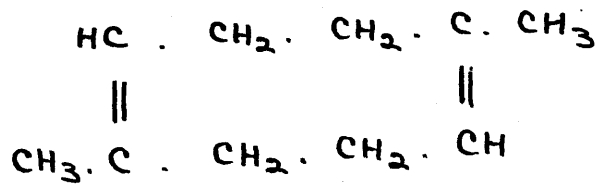
The first empirical formula to be proposed for coautchouc was C_5H_8 and this has been substantiated in many ways since its first promulgation. Caoutchouc is thus an unsaturated hydrocarbon and Gladstone and Hibbert(41), from their measurements of the refractive index of caoutchouc in solution, concluded that it contained three double linkages for each $C_{10}H_{16}$ group in its molecule. Weber, on account of its analogy with the terpenes and Harries for a time, as a result of his study of the ozonide, considered the fundamental grouping of the caoutchouc molecule to be $C_{10}H_{16}$. Recently, Macallum and Whitby(42), have measured the refractive index of a film of caoutchouc and shown that the fundamental unit is C_5H_8 and that, for each C_5H_8 group, there is one double bond, a conclusion borne out by the work of Scheibe and Pummerer(43) on the adsorption spectra and also by the study of the addition products.

From the similarity existing between the empirical formulae of isoprene and caoutchouc, from the occurrence of isoprene as the lowest boiling liquid product of

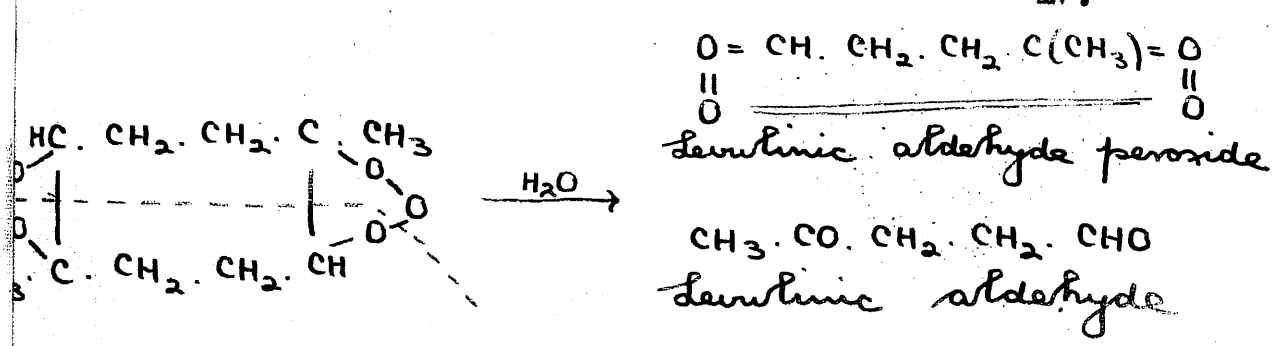
destructive distillation, and from the observation that isoprene can be polymerised to a product closely resembling caoutchouc, the assumption has been made that caoutchouc is a polymer of isoprene. However, how many of these isoprene nuclei go to make up the caoutchouc molecule is still a matter of great uncertainty.

In 1904, Harries(44) began a series of researches on the ozonisation of caoutchouc and made possible a clearer conception of the constitution of the molecule. It is from this work that we have obtained almost our whole knowledge of the nature of the union of the isoprene nuclei and the relative positions of the unsaturated linkages.

He isolated the ozonide (45) as an explosive glassy solid, saturated to bromide. Analysis and molecular weight determinations in glacial acetic acid indicated a molecular formula of $C_{10}H_{16}O_6$. On decomposing his product with water, he obtained levulinic aldehyde, levulinic acid, and some levulinic aldehyde peroxide. From his observations, he assigned to the fundamental unit of caoutchouc the structure



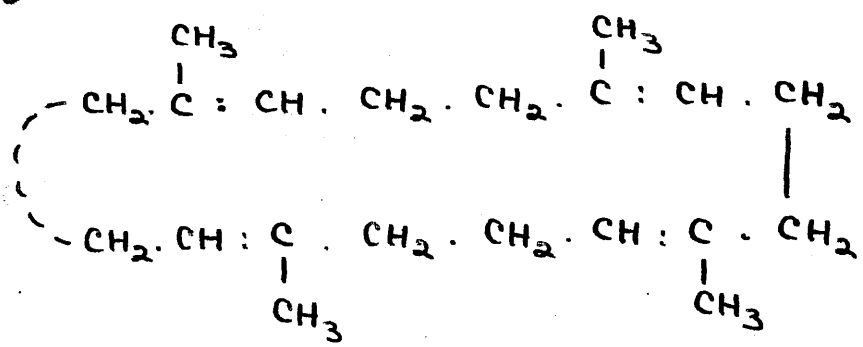
and expressed caoutchouc as $(C_{10}H_{16})_x$. The formation and hydrolysis of the ozonide he represented by the following scheme:-



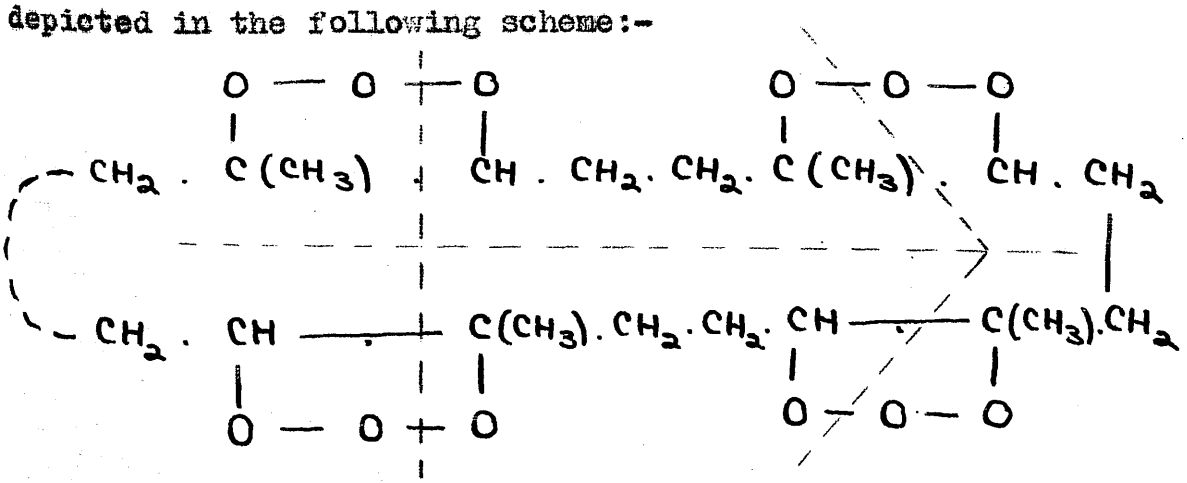
Harries considered that the polymerisation of 1.5-dimethyl-1.5-cyclooctadiene could be explained by the saturation of partial valencies according to Thiele's theory. Thus he thought of caoutchouc in its ordinary state as a loose molecule formed through these residual valencies, the polymer being easily depolymerised to the fundamental unit and becoming capable of reacting as an unsaturated substance.

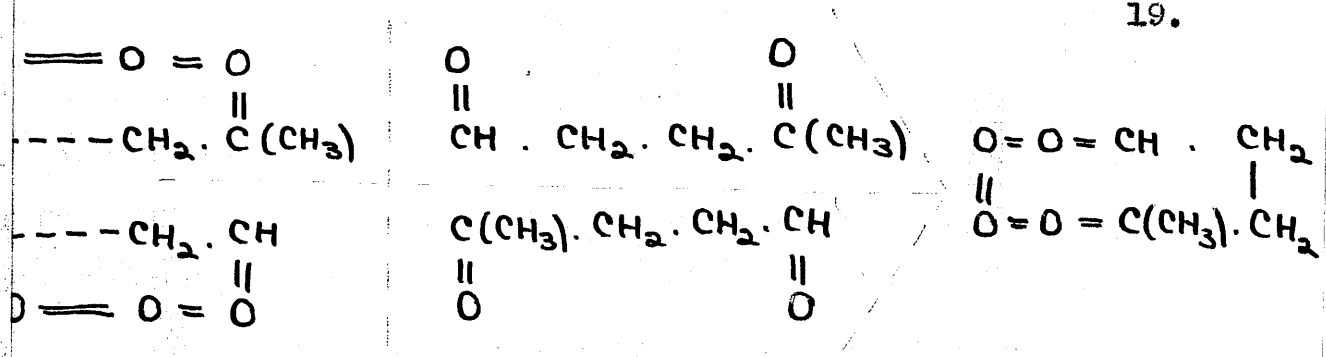
In 1910, Pickles(46) drew attention to the following points which show the unsatisfactory nature of Harries ' cyclooctadiene formula. If the union of the dimethyl-cyclooctadiene nuclei is loose enough for the molecule to be deploymerised by ozone, then the molecule should be broken up, in a similar fashion, by other reagents. Thus bromine ought to react with caoutchouc to give a simple tetrabromide. Instead of this,however, an amorphous substance of the same order of complexity as the original hydrocarbon is formed. Again, if the dimethyl-cyclooctadiene units are chemically united a reduction in unsaturation should result. But the tetrabromide formed corresponds with

the empirical formula $C_{10}H_{16}Br_4$ showing that the complex has the same relative unsaturation as the proposed unit. It was on these grounds that Pickles rejected the 8 carbon ring structure for caoutchouc and, in its place, he suggested a structure formed by the union of an undetermined number of C_5H_8 groups into a large ring as follows:-



Such a formula agrees with the unsaturation value found for caoutchouc and allows of the formation of a derivative, such as the bromide, of complexity the same as that of the parent hydrocarbon. The formation of the ozonide and its hydrolysis to give levulinic aldehyde and its peroxide are depicted in the following scheme:-





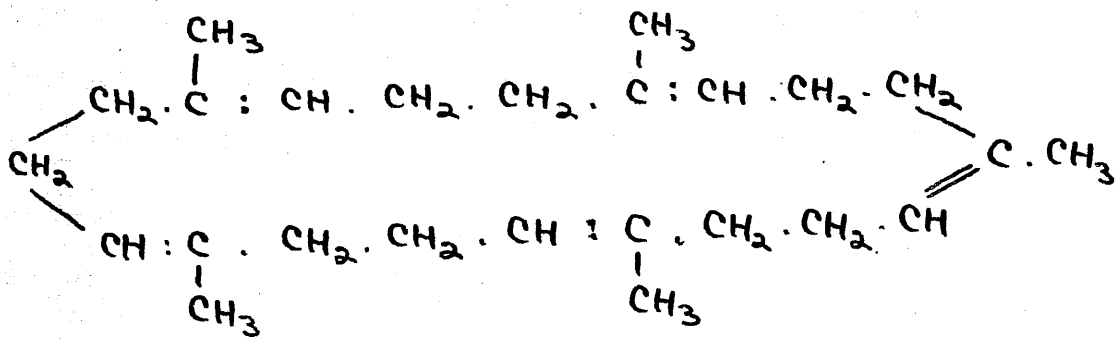
In 1912, Ostromisslenski(47) proposed a similar structure for the caoutchouc molecule. He polymerised vinyl bromide and obtained a product, which he called cauprene bromide, closely resembling the bromide from one of the synthetic rubbers and according to Willstätter(48), quite different from the bromide of cyclooctadiene. He considered that cauprene bromide was a homologue of caoutchouc tetrabromide and proposed the following formulae:-

$$\underbrace{CH_2 . CHBr . CHBr . CH_2 . CH_2 . CHBr . CHBr . CH_2}_{\text{cauprene bromide}}$$

$$\underbrace{CH_2 . CHBr . C(CH_3)Br . CH_2 . CH_2 . CHBr . C(CH_3)Br . CH_2}_{\text{caoutchouc bromide}}$$

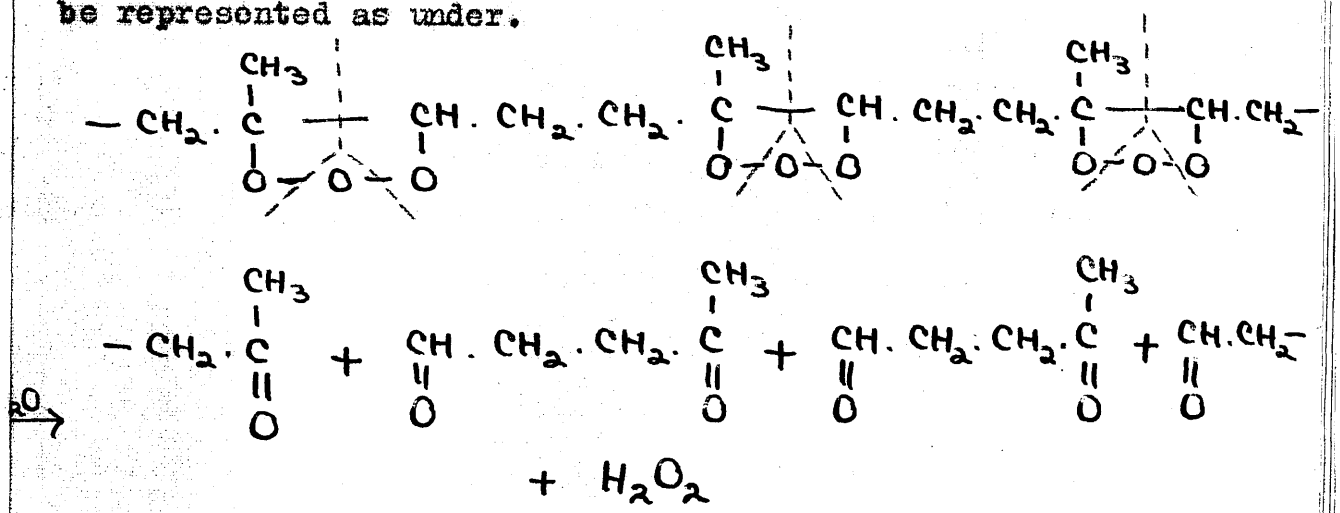
Harries(49), in 1914, published the results of his investigations on the ozonisation of alpha-isorubber, obtained from caoutchouc hydrochloride of the action of pyridine. By hydrolysing the ozonide of this substance, he obtained, in addition to the usual levulinic aldehyde and acid, diacetyl propane, $CH_3CO.CH_2CH_2.CH_2.COCH_3$ and

ether polyketones and ketonic acids. He isolated a triketone containing eleven carbon atoms $C_{11}H_{18}O_3$, undecatrione, and a tetraketone containing fifteen carbon atoms, pentadecatetrone. The presence of diacetylpropane could be explained as being due to the removal of the chlorine of caoutchouc hydrochloride along with a hydrogen atom other than that with which it had been added originally, giving rise to double bonds in the regenerated caoutchouc in positions different from those in the original hydrocarbon. The presence of compounds containing chains of eleven carbon atoms and fifteen carbon atoms could not be explained on the basis of an 8-carbon unit in caoutchouc and Harries, therefore, abandoned his dimethyl-cyclooctadiene structure for one similar to that proposed by Pickles and Ostromisslenski, in which the C_5H_8 groups are united in a large ring, containing a chain of, at least, twenty carbon atoms and represented as follows:-



The formation of the ozonide and its decomposition with the production of levulinic aldehyde and hydrogen peroxide would

be represented as under.



If the hydrochloride of caoutchouc were formed and hydrochloric acid removed again, a rearrangement of the double bonds might occur and give rise to higher ketones amongst the decomposition products of the ozonide of the regenerated caoutchouc. Harries found that when he treated the regenerated caoutchouc successively with hydrochloric acid and pyridine, he obtained a new "Regenerate", the ozonide of which gave, on decomposition with water, an increased yield of high boiling constituents, an indication that a further rearrangement of double linkages had occurred.

Ostromisslenski(50) now came forward with further work on cauprene bromide, the product of polymerisation of vinyl bromide. He considered it to be an isomer of the bromide of synthetic erythrene rubber, which was obtained along with the isomeric cauprene when cauprene bromide was reduced with zinc dust. Also, removal of hydrobromic acid from cauprene bromide and erythrene-rubber

bromide yielded the same product, dehydrocauprene $C_{32}H_{32}$.

$$C_{32}H_{48}Br_{16} - 16\ HBr. = C_{32}H_{32}.$$

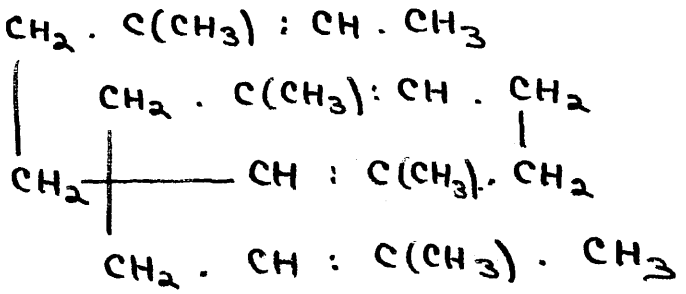
A homologue, $C_{32}H_{24}(CH_3)_8$ was obtained when hydrobromic acid was abstracted from the bromide of natural caoutchouc.

$$C_{32}H_{40}(CH_3)_8\ Br_{16} - 16\ HBr \rightarrow C_{32}H_{24}(CH_3)_8$$

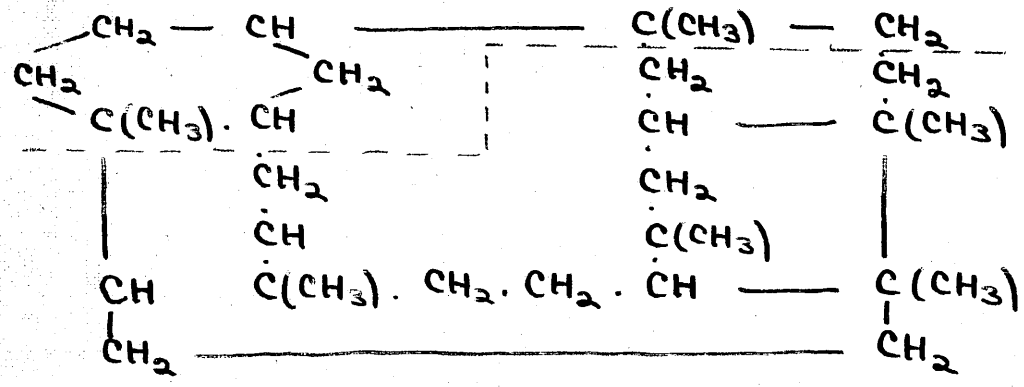
Now, he reasoned that since caoutchouc is obtained by reduction of its bromide, a homologue of the monocyclic cauprene bromide which gives monocyclic cauprene on reduction, then it must be monocyclic also and he suggested a system similar to that of Pickles:

$$\underbrace{CH_2.CH_2.\left[C.(CH_3) : CH.\ CH_2.CH_2\right]_7.C(CH_3):CH}_{C_{40}H_{64}.}$$

Mention must be made of two other formulae which have been proposed for caoutchouc, Kirchhof(51) has suggested an open-chain spiral structure. He believes that the fundamental unit is $C_{10}H_{17}$ and bases this on the discrepancy between earlier analytical results and those required by theory for C_5H_8. The usual explanation given was that the specimen under examination, contained traces of impurities. Kirchhof's proposed formula is as follows:-



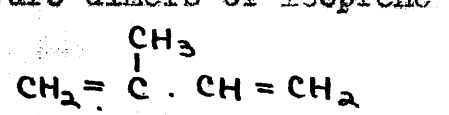
Boswell(52) has proposed another formula quite different from those previously discussed. It is as follows:-



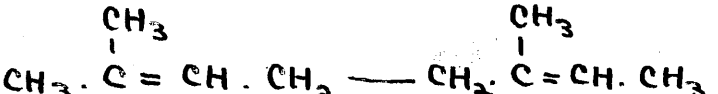
Such a structure is made up of six isoprene units giving $C_{30}H_{48}$ as the caoutchouc molecule. Destructive distillation of such a compound might give dipentene (as shown by dotted line), although never more than 33⅓% by weight of the whole, which is in accordance with actual results. Also, there is one dimethyl-cyclooctadience residue in the molecule and this might yield an ozonide as the result of a fission of the structure under the influence of ozone. The yield of ozonide could only be relatively small (33⅓% of the original caoutchouc). Boswell mentions that this is in accordance with the observations of Olivier(53), who obtained yields of ozonide much less than those required for the conversion of the whole of the caoutchouc taken, such as would be looked for from a structure consisting of isoprene residues fused into a large single ring.

An intsresting piece of work, which provides us with

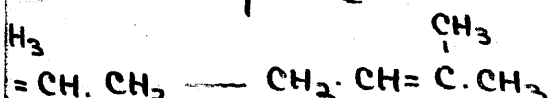
experimental evidence for the polymerisation of isoprene by metals, has been published recently by Midgley and Henne(54). By the action of metallic potassium on isoprene in presence of alcohol, they have obtained a mixture of 2.6-, 2.7-, and 3.6-dimethyl-2.6-octadienes, the three possible dihydro dimers of isoprene



isoprene



2.6-dimethyl-2.6-octadiene



2.4-dimethyl-2.6-octadiene

3.6-dimethyl-2.6-octadiene

This would appear to indicate that synthetic rubber consists of a long chain or large ring of isoprene units joined through their 1 and 4 carbon atoms. The difference between natural and synthetic caoutchouc might be explained by a difference in the position of the methyl groups.

Chemical Properties of Caoutchouc.

The most important derivatives of caoutchouc are addition products, formed at the ordinary temperature and thus very probably retaining the identical structure of the original hydrocarbon without change in the position of the double bonds. The products vary in colour from colourless to yellow. They are amorphous substances of high molecular weight and vary greatly in their behaviour towards solvents.

They are difficult to purify as they do not crystallise and decompose on distillation.

Halogen Products.

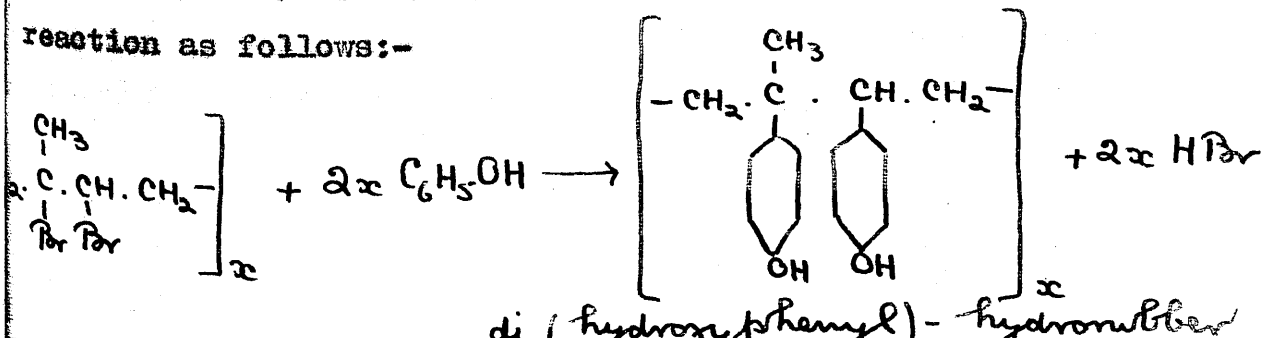
In 1888, Gladstone and Hibbert(41), in an effort to establish the correctness of the conclusion which they had drawn from their refractive index measurements, concerning the unsaturation of caoutchouc, prepared and analysed the halogen addition products. They treated a solution of caoutchouc in chloroform with chlorine and obtained a product which was white and fibrous and analysed for $C_{10}H_{14}Cl_8$. Thus substitution as well as addition had taken place and McGavack (55) has shown that, in the early stages, substitution occurs mainly. Ostromisslenski(56) has reported that caoutchouc chloride is formed when a 9% solution of chlorine in carbon tetrachloride, containing the theoretical amount of chlorine, is mixed with a cold 18% caoutchouc solution in the same solvent. He has given his product the formula $C_{32}H_{40}(CH_3)_8Cl_{16}$ on the assumption that it is cauprene chloride and contains eight isoprene units.

By the action of bromine on a chloroform solution of caoutchouc Gladstone and Hibbert (loc.cit) have obtained a bromine addition compound $C_{10}H_{16}Br_4$, in appearance, very similar to the chloride. With an excess of bromine they obtained a different product $C_{10}H_{16}Br_5$ and they suggested that

this might have been formed by the splitting off of hydrobromic acid from the first-formed $C_{10}H_{16}Br_6$.

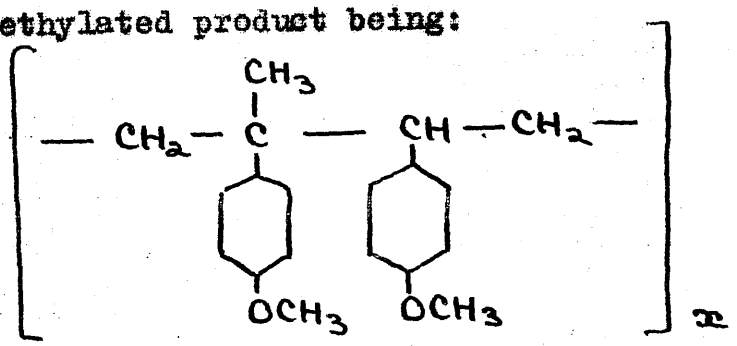
These same workers considered iodine to have only a slight action on caoutchouc in chloroform solution but Weber (57), by using a very large excess of iodine, has obtained an unstable product corresponding to $(C_{10}H_{16}I_3)_x$. Other workers, however, have obtained products of varying composition and sometimes containing oxygen in addition to iodine.

In 1900, Weber (loc.cit) prepared and examined rubber bromide and found that it combined with phenol with the evolution of hydrobromic acid. Analysis of the product corresponded to a "tetroxyphenyl-polyprene" of the formula $C_{10}H_{16}(OC_6H_4)_4$. On account of his inability to get the reaction with phenol-ethers while obtaining similar results to the above with other phenols, he assumed the oxygen to be non-hydroxylic, that is, his product was thought by him to be an ether. But Fisher, Gray and McColm(58) have shown that the phenol product can be methylated easily and therefore there must be hydroxyl groups present. They have represented the reaction as follows:-



di (hydroxyphenyl) - hydrorubber

the methylated product being:



More recently Geiger(59) has prepared the methylated product directly from the phenol ether by the use of ferric chloride as catalyst.

Geiger (loc.cit) has coupled his phenol products with diazotised aromatic amines. The products are amorphous, and of high molecular weight. They contain one diazo-group for each phenyl group.

Phosphonium salts have been prepared by Staudinger, Geiger, and Reuss(60) by the action of triphenyl- and triethylphosphine on rubber bromide. They are saturated and are formed with the evolution of hydrobromic acid so that they must contain cyclic structures.

Action of Hydrohalides.

By treatment of a dilute solution of caoutchouc with moist hydrochloric acid, Weber(57) obtained a colourless elastic addition product which he considered to be the dihydrochloride of the formula $C_{10}H_{16}.2HCl$. Hydrobromic and hydriodic acids also give addition products, $C_{10}H_{16}2HBr$ and $C_{10}H_{16}.2HI$, which, how-

ever, decompose on standing. Hinrichsen, Quensell, and Kindscher(61) prepared the dihydrochloride and dihydrobromide but they did not obtain with hydriodic acid an addition product higher than $C_{10}H_{16}HI$.

Harries(62) heated the above caoutchouc hydrochloride with zinc dust in an ethylene chloride solution which was saturated with hydrochloric acid, and found that the average of several variable analyses for his product agreed with $C_{10}H_{18}$ and he named it "alpha-hydro-rubber". But Staudinger and Widmer(63) have shown that it analyses for $(C_5H_8)_x$. Since it displays an unsaturation very much less than that of the original caoutchouc, they consider that it contains internal ring formations.

Staudinger and Widmer(64) have obtained alkyl derivatives of hydrocaoutchouc from the hydrohalides by the action of zinc methyl and zinc ethyl as follows:-

$$\left[-CH_2\cdot\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}\cdot CH_2\cdot CH_2-\right]_x \xrightarrow{Zn(C_2H_5)_2} \left[-CH_2\cdot\overset{\overset{CH_3}{|}}{\underset{\underset{C_2H_5}{|}}{C}}-CH_2\cdot CH_2-\right]_x + ZnCl_2$$

Hydrogenation.

Attempts to hydrogenate caoutchouc have been successful only in comparatively recent times. Harries(65) and Hinrichsen(66) both used unsuccessfully platinum black as catalyst. It was in 1922, that records of the successful hydrogenation of caoutchou

were made public first by Pummerer and Burkhard(2) and, independently, by Staudinger and Fritschi(27).

Pummerer and Burkhard hydrogenated caoutchouc in hexane solution at the ordinary temperature using, as catalyst, platinum black activated by oxygen after the fashion of Wilstätter and Waldschmitz-Leitz(67). They found that a very pure specimen of caoutchouc was necessary and also that hydrogenation took place only when a very dilute solution (0.2 - 0.6%) of caoutchouc was used. Two atoms of hydrogen per C_5H_8 unit were absorbed and the hydrocaoutchouc isolated had a composition in very close agreement with $(C_5H_{10})_x$. In later work, Pummerer and Koch(3) employed an excess pressure of 0.5 atmosphere of hydrogen and used platinum black which had not been activated previously by oxygen. The hydrocaoutchouc from these experiments was not oxidised on standing in the air, nor was it acted upon by bromine or potassium permanganate. It gave no depression of the melting-point when dissolved in camphor but, after it had been heated for several hours at 200°, followed by 20 minutes at 300°, in an atmosphere of carbon dioxide of 12mm. pressure, it did give a depression which pointed to a molecular weight of 1700. There was no trace of decomposition during the heating so that the change would appear to be one of disaggregation of the hydrocaoutchouc.

When the hydrocaoutchouc was distilled at 350° under 1mm. pressure of hydrogen, it yielded a saturated hydrocarbon $C_{50}H_{100}$ of molecular weight 714 in camphor. The residue, which was saturated and colourless, had a composition corresponding to $(C_5H_{10})_x$ and a molecular weight in camphor of 1500.

Staudinger and Fritschi employed high temperatures and pressures in their hydrogenation of caoutchouc. They heated purified caoutchouc, impregnated with colloidal platinum, for 10 hours at 270° in an atmosphere of hydrogen of 93 atmospheres pressure. The hydrocaoutchouc was isolated as a colourless, transparent, inelastic mass having typical colloidal properties. Analyses agreed closely with $(C_5H_{10})_x$. It was stable to bromine addition, although on standing in the sunlight hydrobromic acid was evolved and bromine absorbed slowly. When bromination was allowed to go to completion and the bromine then removed as hydrobromic acid, a regenerated caoutchouc was obtained.

Decomposition of the hydrocaoutchouc at 350-400° under 1mm. pressure resulted in the formation of a series of hydrocarbons of the type $(C_5H_{10})_x$, each possessing one double bond. Only a small residue (0.6%) remained and the lowest boiling product identified was methylethylethylene, C_5H_{10} (5%). The highest member isolated was $C_{50}H_{100}$ (24%), which indicated a

high M.W. for hydrocaoutchouc.

Action of the Oxides of Nitrogen.

The formation of a compound of the nature of a nitrosite of caoutchouc was first described by Harries(68), who passed nitrogen trioxide through a solution of caoutchouc in petroleum-ether. The product varied according to whether moist or dry reagents were used, but the chief product seemed to be "nitrosite C", corresponding to $C_{10}H_{15}N_3O_7$. It was oxidised by potassium permanganate to a mixture of fatty acids consisting chiefly of succinic and oxalic acids.

A nitrosate of caoutchouc was obtained by Weber(69) by passing a stream of nitrogen peroxide through a benzene solution of caoutchouc. The product was a yellow, acetone-soluble powder, $C_{10}H_{16}N_2O_4$, having acidic properties and yielding sodium and silver salts. Alexander(70) has produced results confirming those of Weber but other workers have shown that oxidation takes place as well as the addition of nitrogen peroxide. Recently, Emden(71) has studied the reaction. He mixed cold solutions of nitrogen peroxide and caoutchouc in carbon tetrachloride and isolated a colourless product which dissolved only slowly in aqueous caustic soda and in acetone. When water was added to the reddish-brown acetone solution a pale yellow substance, easily soluble in acetone, was

precipitated. Analyses of the original product agreed with $C_{10}H_{16}N_2O_6$ and showed that addition of nitrogen peroxide had been accompanied by oxidation.

Action of Nitric Acid.

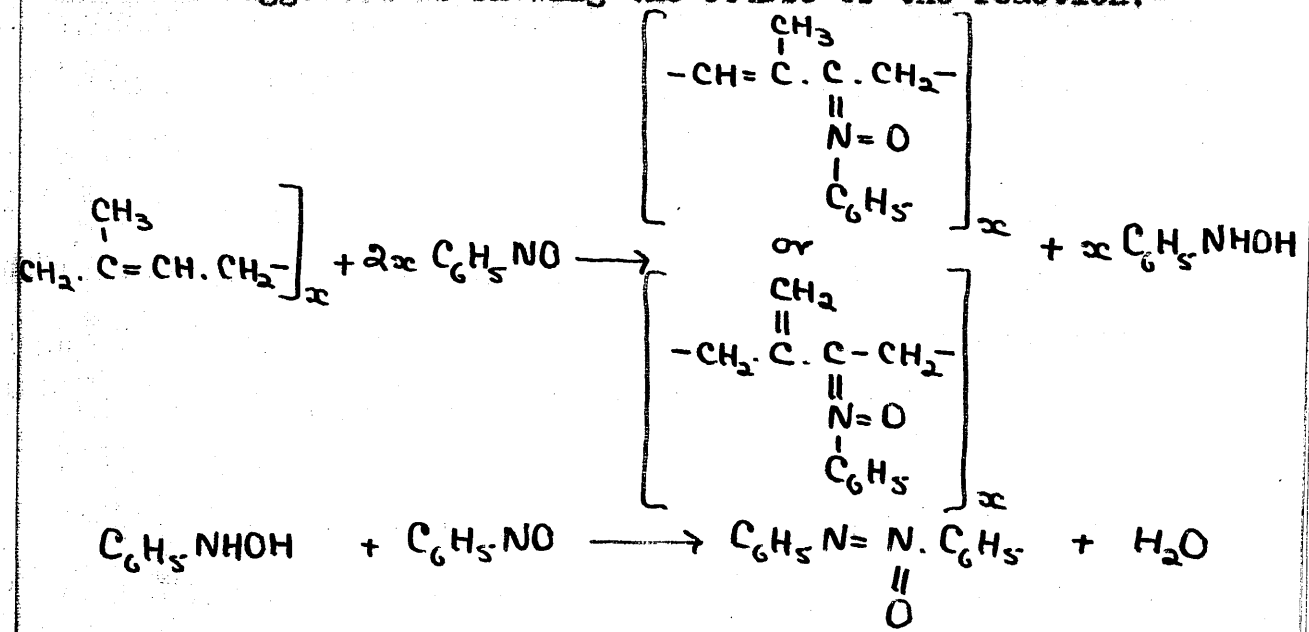
Ditmar(72) was the first to study the product of the action of concentrated nitric acid on caoutchouc. He isolated an acidic substance which could be reduced by sodium methoxide. Harries(73) substantiated these observations of Ditmar who, later(74), proposed that the substance was 5.6-dinitro-2.5-dihydrocumic acid $C_3H_7(C_6H_4)(NO_2)_2.COOH$.

More recently Fisher(75) has isolated a different product from the reaction between concentrated nitric acid in excess and a 5% solution of caoutchouc in carbon tetrachloride. It is bright yellow in colour, and differs from Ditmar's product in being insoluble in sodium carbonate solution. The formula assigned to it is $(C_5H_7NO_2)_x$. It is probably a nitro-polycyclo-caoutchouc since the unsaturation is only 24.8% of that calculated for a nitro-caoutchouc.

Action of Nitroso Compounds.

In 1915, Allesandri(76) obtained a product $C_{58}H_{61}O_9N_5$ by treating caoutchouc with nitrosobenzene. However, a more recent report on the reaction has been published by Bruni and Geiger(77) and several derivatives are mentioned in it. They have found that when the proportion is 3 mols of nitrosobenzene

per C_5H_8 group a product of the composition $C_{11}H_{11}ON$ is formed. It is unsaturated since it forms an addition product with bromine, $C_{11}H_{11}ONBr_2$. The following scheme has been suggested as showing the course of the reaction:-



Azoxybenzene has actually been obtained as a product of the reaction. The nitrone has the properties of a colloid and gives rise to a phenylhydrazone, which must be considered, along with the nitrone, a derivative of isocaoutchouc since the position of the double bond is different from that in the original caoutchouc.

These observations have been confirmed by Pummerer, Andriessen, and Gündel(78) who found the M.W. of the nitrone in benzene and in nitrobenzene to be 1200-1400. The M.W, of $(C_{11}H_{11}ON)_8$ would be 1384. Corresponding products have been

obtained from other nitroso compounds e.g. the 3 nitrosotoluenes and o-nitrosoanisole.

Action of Chromyl Chloride.

Chromyl chloride and the terpenes react to form additive compounds $C_{10}H_{16}{}^{2}CrO_2Cl_2$ which are decomposed by water into volatile aldehydes and ketones. The similarity existing between the addition products of the terpenes and those of caoutchouc led Spence and Galletly(79) to study the action of chromyl chloride on caoutchouc. They isolated an amorphous brown substance which resembled closely the corresponding terpene addition compounds and had the same composition. However, decomposition with water produced products different from those usually obtained from terpenes. Two main products were separated. One was soluble in acetone and alcohol and possessed pronounced aldehydic properties while the other was insoluble in all usual organic solvents and was an acid of indefinite composition containing chromium and chlorine. Robertson and Mair(80) have repeated the work and verified the observations.

Action of Metallic Salts.

Bruson, Sebrell, and Calvert(81) have recorded the formation of additive compounds when caoutchouc solutions are treated with stannic, titanic, ferric, or antimonic chlorides. The product with stannic chloride has the empirical composition $(C_5H_8)_{10}.SnCl_4$

$SnCl_4$ and on treatment with alcohol, splits off stannic chloride with the formation of a polymerised or polycyclic caoutchouc. Two isomeric compounds are formed in the ratio of 3:1 and correspond with "sol" and "gel" rubbers. Titanic chloride yields analogous products but ferric chloride and antimonic chloride give only the insoluble variety even when "sol" rubber is used.

Action of Sulphur and Sulphur Monochloride.

Treatment of rubber with sulphur under certain favourable conditions is called vulcanisation and greatly enhances its qualities of strength, resiliency, elasticity, resistance to the action of solvents, and increases considerably its durability. The discovery of this process made possible its wide application in industry.

At the ordinary temperature sulphur does not react with caoutchouc but when a cumene solution of caoutchouc is heated for several hours at 170° with an excess of sulphur, a completely sulphurised caoutchouc, $(C_5H_8S)_x$, is obtained as a brown insoluble powder(82).

Sulphur monochloride, according to Weber(35), forms a compound with caoutchouc expressed by $C_{10}H_{16}.S_2Cl_2$. But Hinrichsen and Kindscher(82) claim that the amount of reagent added indicates the formula $(C_{10}H_{16}.SCl)_x$. Kirchhof(83) passed sulphur monochloride vapour into a solution of caoutchouc

and, from his analysis of the escaping gases, he calculated that a compound, intermediate between the above compounds, had been formed. He considered it probable that Weber's compound had been the primary product and had yielded the others by partial decomposition.

Recently, Meyer and Mark(84) have compared the reaction with the "mustard gas" reaction, in which sulphur monochloride reacts with ethylene as follows:-

$$2CH_2 : CH_2 + S_2CL_2 \qquad (CH_2Cl.CH_2)_2S + S.$$

They have produced results agreeing fairly well with a compound of the composition, $C_{10}H_{16}SCl_2$ which would be required if the reaction were analogous to the above.

Action of Oxygen and Oxidising Agents.

In 1865, Spiller(85) examined the products from perished rubber. He extracted with benzene a perished waterproof sheet, consisting of a fabric coated with unvulcanised rubber, and from the extract, obtained a yellow resinous substance, soluble in methyl alcohol, chloroform and in dilute aqueous alkalies, from which it was reprecipitated by acids. Also it was insoluble in carbon disulphide and turpentine and sparingly soluble in ether and was therefore quite different from the original rubber and it has been given the name "Spiller's resin". Values obtained from analyses corresponded with $C_{30}H_{48}O_{10}$.

It was not until 1906, that further work in this particular branch of the subject was published. In that year, Herbst(86) reported the results of experiments, in which he passed, for 140 hours, a current of air through a boiling benzene solution of rubber. He isolated two main products. One was a reddish brown syrup of the composition $C_{10}H_{16}O$ and soluble in petroleum ether and the other, which was obtained in small amount only, was a yellow solid, amorphous and friable, of the composition $C_{10}H_{16}O_3$ and insoluble in petroleum-ether.

In 1912, Peachey(87) measured the amount of oxygen absorbed by carefully purified caoutchouc in the form of thin films deposited on the inside of a flask, and found that two mols. were absorbed for each $C_{10}H_{16}$ group. This was confirmed later by Peachey and Leon(88) who observed also that carbon dioxide, to the extent of 1 mol. per $C_{40}H_{64}$, was produced during the reaction. The resulting material was extracted with alcohol and, after fractional precipitation from various solvents, four substances were obtained: (1) a fawn coloured amorphous substance of weakly acidic properties, insoluble in petroleum ether and in carbon disulphide, and soluble in alcohol and acetone. Composition $C_6H_9O_2$. (2) a yellow resin, neutral and soluble in the usual organic solvents. Composition $C_{16}H_{26}O_3$. (3) a brown amorphous solid, insoluble in organic solvents, and soluble in dilute alkalies. Composition $C_{11}H_{16}O_4$. (4) a

reddish brown amorphous solid, insoluble in organic solvents and alkalies, different from (1). Composition $C_6H_9O_2$. No explanation has been given of the relationship between these compounds or mixtures and the original hydrocarbon.

It would appear that there is a progressive addition of oxygen and it has been suggested by Kirchhof(89) and, later, by Ostwald(90) that air oxidation is a process of autoxidation brought about by means of unstable peroxides. The presence of such peroxides has been observed during the reaction.

In 1922, Boswell and his workers(91) obtained two products as a result of exposing pure caoutchouc to the action of atmospheric oxygen in bright sunlight for three months. One had properties very similar to those of caoutchouc and analysed for $C_{10}H_{16}O$ whereas the other was a hard brittle substance, insoluble in carbon disulphide and of composition $C_{25}H_{40}O_9$.

Before passing on to another type of oxidation, it must be noted that the presence of levulinic aldehyde in "tacky" rubber, formed by exposure to air and light, has been observed by Gorter(92) and the observation has been verified by Bruni and Pelizzola(93) and by Whitby(94) who prepared its pyridazine derivative.

The action of potassium permanganate on caoutchouc was studied by Harries(44) who, using a 2.5% solution of the

reagent, found that only a slight reaction took place. The main result was that considerable disaggregation of the caoutchouc occurred. However, Boswell, Hambleton, Parker and McLaughlin(91), who used a 7.5% permanganate solution with a 4% solution of caoutchouc in carbon tetrachloride, obtained a product of approximate composition $C_{25}H_{40}O$, very closely resembling caoutchouc in solubility. On exposure to the air it absorbed oxygen and yielded a substance of the composition $C_{25}H_{40}O_2$. More recently Robertson and Mair(80) have investigated the action on caoutchouc of neutral and alkaline potassium permanganate solutions of different concentrations and have isolated both acidic and neutral products. Amongst the acid products formic, acetic, oxalic and levulinic acids were recognised and, in addition, complex colloidal acids of a resinous nature were obtained. The neutral products, which were all insoluble in alcohol and acetone, showed an absorption of oxygen approximately proportional to the concentration of the oxidising agent. The formulae assigned to the products were $C_{35}H_{56}O_4$, $C_{30}H_{50}O_5$, $C_{26}H_{42}O_6$; $C_{24}H_{38}O_6$, $C_{20}H_{32}O_5$, $C_{30}H_{48}O_{10}$, etc. giving a range of oxygen to C_5H_8 ratios of from 1:9 to 5:3.

Hydrogen peroxide was used by Boswell(91) to oxidise caoutchouc in glacial acetic acid carbon tetrachloride solution. He isolated as primary product of the reaction a compound

$C_{30}H_{48}O$, which absorbed oxygen on exposure to the air with the formation of a substance $C_{25}H_{40}O_2$. Since then Robertson and Mair(80) have carried out the oxidation of caoutchouc in a glacial acetic acid-chloroform solution and have obtained as main product a colourless amorphous substance, neutral in character, possessing alcoholic properties and having a composition corresponding to $C_{59}H_{102}O_{16}$.

Treatment of caoutchouc with perbenzoic acid was found by Pummerer and Burkhard(2) to yield a colourless product of the nature of an oxide. It was insoluble in organic solvents and gave analyses for $(C_5H_8O)_x$. It is worthy of mention here that the existence of such a derivative would seem to provide evidence in favour of the view that C_5H_8 should be regarded as the fundamental unit in the caoutchouc molecule and not $C_{10}H_{16}$.

Action of Sulphuric Acid.

The action of concentrated sulphuric acid on a benzene solution of caoutchouc was studied by Harries(65) who obtained an amorphous product which was insoluble in benzene. He could not free his product from ash but, nevertheless, he considered it to be a higher polymeride of caoutchouc. Marquis and Heim (95) treated a chloroform solution of caoutchouc with strong sulphuric acid and obtained a colourless amorphous substance soluble in benzene and chloroform and containing no sulphur. Since the composition was not represented exactly by C_5H_8

addition of the elements of water or oxidation may have occurred. By prolonging the time of the reaction an insoluble product was obtained. A few years later, Kirchhof(96) treated a carbon tetrachloride solution of caoutchouc with strong sulphuric acid and isolated a hydrocarbon without any of the characteristics of caoutchouc and apparently of the composition $C_{10}H_{15}$. It yielded additive compounds with bromine and sulphur, $C_{20}H_{30}Br_2$ and $C_{20}H_{30}S$, indicating an unsaturation of only one-quarter that of caoutchouc. Kirchhof suggested that the decrease in unsaturation might have been due to mutual saturation of double bonds with the formation of tetramethylene rings. He later considered another type of cyclisation to have occurred(97). By prolonged treatment of a benzene solution of caoutchouc with concentrated sulphuric acid in the cold, the same worker (loc.cit) obtained a red acetone-soluble product of the nature of an aldehydic acid. It had the composition $C_{20}H_{30}O_3$ and yielded a phenylhydrazone of M.P. 120-124°. Kirchhof suggested for it a structure consisting of a spiral chain with a -CHO group at one end and a -COOH group at the other end.

B. Gutta-Percha.

---oOo---

Source.

Gutta percha is the coagulated latex obtained from several trees belonging to the botanical family Sapotaceae. The most important sources are the Palaquium gutta and the Palaquium oblongifolia and these are almost entirely confined to the Malay Peninsula and Archipelago. Allied trees of the same genus and family yield similar but inferior products.

The latex is collected by a system of tapping similar to that employed in the collection of rubber latex. A number of incisions are made in the bark of the tree and the latex is allowed to run from these into suitably placed receivers. A difficulty is experienced here which is not encountered in the tapping of rubber trees. The gutta percha latex flows very much more slowly and coagulates more quickly than the rubber latex with the result that the yield per tapping is very much less. This led the Malays to adopt for the extraction of the latex a method which involved the total destruction of the trees. They cut down the trees and then made at short intervals in the bark wide incisions extending right round the trunk of the tree. Now, however, every effort is made to reduce the extent of the practice as much as possible.

The method of coagulation, by addition of acid, common on rubber plantations, is not employed for the coagulation of gutta latex. Coagulation of this last substance is induced by gently heating in suitable vessels after which treatment the coagulated gutta-percha is boiled in water and moulded into various shapes.

Physical Properties.

The blocks of gutta-percha which appear on the market have a dirty greyish appearance and are just soft enough to be indented by the nail. The material has a fibrous texture and, unlike rubber, it is almost destitute of elasticity. It possesses the characteristic property of becoming soft and plastic on immersion in hot water and hardening without becoming brittle on cooling again. In the soft and plastic state it can be moulded into any desired shape, rolled into sheets, or drawn into wire, and it will retain its new form when cold. In the possession of this property it differs greatly from rubber which, when it is heated under the same conditions, becomes sticky and moderately plastic but retains its resiliency.

Chemical Composition.

Gutta-percha resembles rubber in being a mixture of a hydrocarbon $(C_5H_8)_n$ with resinous bodies and a small quantity of insoluble material. The proportion of resin in gutta-percha

is, however, very much greater than in rubber and it is to this increased resin content that many of the characteristic properties of gutta-percha are due.

The hydrocarbon is separated from the other constituents by extracting the resins with acetone, dissolving the residual hydrocarbon in benzene, filtering from insoluble material, and reprecipitation by means of alcohol. The hydrocarbon, thus purified, is a colourless inelastic solid of a leathery consistency and possessing, in an enhanced degree, most of the properties of the crude material. On immersion in hot water it becomes soft and plastic and readily moulded; on cooling it becomes hard but not brittle and retains the shape given to it when soft. When distilled at a high temperature it yields a distillate similar to that obtained when caoutchouc is submitted to destructive distillation, namely, a mixture of liquid hydrocarbons consisting of isoprene C_5H_8 and higher boiling hydrocarbons including $C_{10}H_{16}$ and $C_{30}H_{48}$.

The oxygenated resinous constituents which are in association with the above hydrocarbon have been divided into two portions: (1) a white crystalline resin, soluble in hot but insoluble in cold alcohol and (2) a yellow amorphous resin insoluble in hot alcohol. Such a separation was first carried out in 1852 by Payen who gave them the names alban and fluavil respectively. In 1892, Oesterle(98) isolated a fourth

constituent having the composition C 86.4% H 12%, which he termed guttan. It was unstable and was converted into gutta by repeated dissolution and reprecipitation. In 1903, Tschirch(99) obtained a further separation of the alban fraction. By fractional crystallisation from alcohol he separated it into spherite-alban $C_{30}H_{44}O_2$, m.p. 152° soluble in hot alcohol, and crystal-alban, $C_{60}H_{80}O_3$, m.p. 228° soluble only with difficulty even in boiling alcohol. van Romburgh (100) showed later that Tschirch's crystal-alban was an ester of cinnamic acid and lupeol (101).

Chemical Properties.

Halogen Compounds.

By passing pure dry chlorine into a solution of gutta in dried carbon tetrachloride until saturated, Caspari(102) obtained a compound approximating to the formula $C_{20}H_{36}Cl_4$ which indicated that more substitution than addition had occurred. Bromine, acting on a solution of gutta in dried chloroform, did not exhibit the same tendency to substitute there being only a slight disengagement of hydrobromic acid while the product was of the composition $C_{30}H_{46}Br_{10}$. A product of the composition $C_{10}H_{16}Br_4$ was obtained by Ramsay, Chick, and Collingridge(103) by the action of bromine on gutta. Iodine did not give definite products when it was allowed to react with a dry chloroform solution of gutta.

Gaseous hydrochloric acid reacted with a benzene solution of gutta to give a compound corresponding with $C_{30}H_{45}.5HCl$.

Quite recently, Geiger(59) has obtained condensation products of gutta bromide with various phenols using ferric chloride as catalyst. With ordinary phenol he obtained bis-(p-hydroxyphenyl)-hydrogutta-percha, a brown amorphous substance soluble in alkalies and yielding a yellowish-brown dibenzoate of m.p. 190.5°, of high M.W. m-Cresol and resorcinol gave similar products.

Oxides of Nitrogen.

Caspari found that when gutta percha was treated with nitrogen peroxide the first product was a green gelatinous precipitate which dried to a horny mass of variable composition. Further treatment yielded a yellow clot which, when dissolved in acetone and reprecipitated by ether gave a buff-coloured powder, $C_{10}H_{16}N_2O_4$, soluble in acetone and ethyl acetate, also in caustic alkalies but insoluble in ammonia. Prolonged treatment converted this substance with evolution of heat and bubbles of a gas, to a saffron yellow powder soluble in acetone, ethyl acetate, alkalies, and ammonia. It was given the formula $C_{10}H_{15}N_3O_7$ and was considered to be identical with Harries' "nitrosite C" of the same formula.

When he treated gutta with nitric oxide, the same worker

obtained a product in which the nitrogen and oxygen were not in the proportion in which they were originally supplied. He explained this by assuming that addition had been accompanied by oxidation.

Nitric acid in reaction with gutta yielded a yellow amorphous body to which was assigned the formula $C_{15}H_{21}N_4O_{11}$, the same as that given to it by Harries.

By the action of nitroso bodies on gutta, Bruni and Geiger(77) have prepared compounds corresponding to the derivatives of isocaoutchouc which they obtained by a similar reaction. They have prepared both isogutta-percha-nitrosobenzene and its bromide by a method the same as that employed in the preparation of the corresponding derivatives of isocaoutchouc (loc.cit).

Oxidation.

From the oxidation of an ethereal solution of gutta by means of atmospheric oxygen, Ramsay and his workers(103) isolated a substance of nearly the same composition as alban, $C_{17}H_{26}O$. When they carried out the oxidation in toluene solution the reaction took a different course and resulted in the formation of a sticky solid, $C_{12}H_{24}O_4$, which decomposed when distilled under reduced pressure yielding a mixture of gaseous products and a yellow oil, $C_{12}H_{20}O_3$, of the odour of peppermint.

Harries(45) found that on treatment of a chloroform solution of gutta with ozone an ozonide $C_{10}H_{16}O_6$ was formed which gave, on decomposition with steam a mixture of levulinic aldehyde and acid and levulinic aldehyde peroxide like that from caoutchouc ozonide but in different proportions. This led Harries to the conclusion that caoutchouc and gutta percha are identical.

C. Balata.

-oOo-

Source.

Balata, which resembles gutta percha very closely and is the best natural substitute for it, is the product obtained by coagulating the latex of the "bullet" tree, (Mimusops globosa), a very close relative of the gutta-percha tree. It belongs to the same botanical family as the latter, the Sapotaceae, and is native to the West Indies, Venezuela, British, Dutch, and French Guiana, and to Brazil north of the Amazon.

Originally the tree was felled before collection of the latex, but the practice has been almost entirely eradicated and now, latex is obtained by the usual method of periodical tapping. After collection, the latex is transferred to shallow wooden vessels in which it is exposed to the air until coagulation has been brought about by the heat of the sun. By this means balata is obtained in sheets. Coagulation is often induced by boiling the latex but never by the acid process commonly employed to coagulate rubber latex.

Physical Properties.

Balata resembles gutta percha very closely in physical properties. It is an inelastic solid, like the latter, and may be grey, pinkish, or brown in colour. When immersed in

hot water it behaves as gutta percha does; becoming soft and plastic and, on cooling, hardening again without becoming brittle.

Chemical Composition.

Balata has a chemical composition analogous to that of gutta percha. It consists principally of a hydrocarbon of the empirical formula C_5H_8 associated with resins; the commercial product contains also variable amounts of insoluble matter and moisture. Balata contains a much higher proportion of resins than good gutta percha and, consequently, it is inferior in quality to the latter. When balata is compared with a gutta-percha containing the same proportion of resin, it is found to be a little softer and more flexible.

The hydrocarbon of balata, which is purified in the same way as that of gutta percha, has very similar properties to the gutta and, as a matter of fact, is considered to be identical with it.

The resins of balata are analogous to those of gutta percha consisting of (1) balalban and (2) balafluavil in the proportion, according to Obach, of 2 parts of the former to 3 parts of the latter. Tschirch and Schereschewski(104), by fractional crystallisation of the balalban from alcohol obtained a further separation into readily soluble β- balalban,

$C_{27}H_{44}O_2$ or $C_{27}H_{46}O_2$ of m.p. 108-9° crystallising in lustrous scales, and sparingly soluble α-balalban, $C_{27}H_{42}O_2$ of m.p. 230-1° crystallising in needles. From the alcoholic extract, from which the balalban had separated, they obtained a sticky amorphous substance by pouring it into dilute hydrochloric acid. It was balafluavil of the composition $C_{10}H_{18}O$. Two years later Cohen(105) showed that the α-balalban mentioned above was identical with β-amyrin acetate.

Chemical Properties.

The chemical relationship existing between the hydrocarbons of balata and gutta is a very close one, so close indeed that they have been considered to be identical. Both of them analyse for C_5H_8 and each contains one double bond per C_5H_8 unit of its molecule.

When balata is treated with chlorine, bromine, or iodine under the same conditions as gutta, previously reported, the products are very similar if not identical with those obtained with the latter substance. Here again, chlorine shows a greater tendency to substitute than does bromine; and iodine, again, does not give any definite product, a large proportion of the iodine originally absorbed being removed when it is brought into solution and reprecipitated with alcohol. Oxides of nitrogen also yield products of the same composition as those from gutta, nitrogen peroxide giving, after protracted

actions a compound $C_{10}H_{15}N_3O_7$ corresponding with Harries' "nitrosite C" and nitric oxide a yellow amorphous substance $C_{10}H_{16}NO_2$ in the formation of which addition seems to have been accompanied by a certain amount of oxidation. Nitric acid was found to yield a yellow amorphous compound of composition corresponding with Harries' formula $C_{15}H_{21}N_4O_{11}$.

Bruson, Sebrell and Calvert(81) have reported the formation of an addition product of stannic chloride and balata corresponding to the addition products of caoutchouc with metallic chlorides. On being treated with alcohol, such a compound splits off stannic chloride, just as the caoutchouc-stannic chloride compound does, and yields a benzene-soluble polymer of balata, softening at 200° and decomposing at 250°.

Balata, purified by elimination of resins, becomes altered on exposure to air and light, and there is formed a resin of a different nature from the resins originally present. This alteration of balata by air and light takes place less readily than that of gutta. Dawson and Porritt(106) have studied the oxidation of balata by atmospheric oxygen. They purified Venezuelan sheet balata by extraction with acetone and separation from a clear benzene solution by addition of alcohol and exposed it to a current of air at the ordinary temperature. The oxidation followed an autocatalytic course

and yielded a final product having the approximate composition $C_{10}H_{16}O_3$. There was also produced a small amount of formic acid but no carbon dioxide. Assuming that 1 carbon atom in every $(C_{10}H_{16})_n$ was converted into formic acid, they concluded that n = 112.

. . . . . .

When consideration is taken of the length of time for which rubber and its substitutes have been known, the diverse uses to which they have been put, and the important place which they have taken amongst the industries of the world, then it would seem that the study of these substances has been subjected to an unwarranted neglect. Forth, while many reagents, the variety of which is rather remarkable, have been utilised in attempts to elucidate their constitution, yet there have been practically no researches of a consecutive character, possibly due to the exceedingly unattractive nature of the products which are quite generally obtained from them. While it seems evident that caoutchouc, gutta percha, and balata are closely related hydrocarbons consisting of C_5H_8 nuclei built up to form a large ring or long chain, the size of the molecules, the method of joining up these nuclei, and the immediate relationship of the three substances, whether they are isomers or polymers or in a different state of aggregation is, at the moment, still fairly obscure.

PART II - EXPERIMENTAL.

It was proposed in this study of the behaviour of caoutchouc, gutta.percha, and balata towards oxidising agents to submit these substances and corresponding derivatives of them to, as nearly as possible, identical reaction conditions. On account of the parallel nature of the courses of the reactions and the very close similarity in properties of the products from each of the three sources it has been found possible to treat the various derivatives at corresponding stages of the work in an exactly similar fashion. So, when a description of a method of preparation or isolation of a derivative is given without mention or reference to a particular branch, then it is to be understood that it applies to all three cases.

Corresponding derivatives from the three sources were almost indistinguishable in appearance and in their behaviour towards solvents and only by quantitative analyses were they shown to be quite distinct. The results of such analyses will be recorded in this part of the thesis but no reference will be made here to the possible explanation of them. A new complete section will be devoted to the proposed interpretation of these results.

Purification of the Raw Materials.

The standard method, due to Harries, was adopted for the purification of the caoutchouc. The material used was a very fine specimen of crepe rubber in the form of thin sheets of a very pale yellow colour. Resins were removed by extraction with acetone for 12 hours in a Soxhlet apparatus. The hydrocarbon was then dissolved in benzene, the solution filtered, and the caoutchouc reprecipitated by the addition of alcohol. The final product was almost colourless and considered to be of sufficient purity for the work proposed.

At first the above method was employed for the purification of the gutta-percha and balata hydrocarbons but later a method rather different was adopted. About 20-25 grams of the crude material, cut up into small pieces, was treated in a conical flask with 400-500cc. of boiling $^{60}/_{80}$ petroleum ether and the mixture kept at 40° until most of the insoluble material had settled to the bottom of the flask. Invariably a longer time was necessary for settling with gutta than with balata and even with different specimens of the same raw material the period varied greatly. When the supernatant liquid was almost free from suspended matter, the mixture was allowed to cool. Lowering of the temperature brought about the separation of the hydrocarbon which had dissolved in the hot petroleum ether. It was a colourless pasty mass and was

easily separated mechanically from the insoluble residue at the bottom of the flask and by filtration from the resins in solution in the cold petroleum ether. The filtered hydrocarbon was submitted to several successive treatments similar to the above, using fresh petroleum-ether each time. When found necessary, kaolin was added to the solution to facilitate settling of suspended matter. The hydrocarbon was dissolved in benzene and reprecipitated with alcohol. It was extracted with boiling alcohol to remove any air oxidation product present and finally, dried in vacuo. The final gutta and balata products were very similar in appearance. They were colourless tough solids, transparent in hot alcohol. On exposure to the air they were readily oxidised and therefore were kept before use in an atmosphere of carbon dioxide.

Oxidation of the Hydrocarbons.

Hydrogen peroxide was chosen as oxidising agent because of the mildness of its action which might be expected to yield products containing the parent molecular structures without any considerable degradation. Henderson and his workers (J.C.S. 1911, 99, 1539; 1912, 101, 2288, etc.) have elaborated a method of oxidation with hydrogen peroxide which they have used to great advantage in their work on alkaloids and terpenes and this method has been modified by Robertson and Mair(80) to suit the requirements of caoutchouc. In the original method

the terpene hydrocarbon was dissolved in glacial acetic acid and mixed with sufficient 100-volume hydrogen peroxide to yield a proportion of 2 mols of H_2O_2 per $C_{10}H_{16}$ of hydrocarbon. Since the oxidation seems to take place through the formation and subsequent decomposition of peracetic acid and since caoutchouc is insoluble in glacial acetic acid, the later workers employed a solution of caoutchouc in chloroform and added to that glacial acetic acid. In this research also chloroform was used as solvent for the hydrocarbons and the proportions of ingredients in the reaction mixture of Robertson and Mair were retained in the earlier preparations but were altered later to yield a proportion of 3 mols. of H_2O_2 per $C_{10}H_{16}$. The final reaction mixture was as follows:-

25 gm. hydrocarbon
350 cc. chloroform
250 cc. glacial acetic acid.
55 cc. perhydrol (100 vol. H_2O_2).

To the solution of hydrocarbon in chloroform was added, in small quantities and with vigorous shaking, the glacial acetic acid. Addition of the acid caused reprecipitation of some of the hydrocarbon but the precipitated material redissolved with the shaking until 190-200cc. of the acid had been added beyond which point the reprecipitated hydrocarbon remained undissolved. Addition of the perhydrol caused a further precipitation of hydrocarbon. The reaction mixture consisted

of an upper layer of white clotted hydrocarbon floating in a mobile liquid, of a very pale yellow colour in the case of caoutchouc and colourless in the gutta and balata oxidations, and it was kept for several days at a temperature of 50° according to the instructions of the earlier workers. Since the products from several such oxidations carried out at that temperature gave on analysis, varying results, a series of oxidations was carried through at different temperatures to find out if a more constant product could be obtained. At room temperature, the reaction did take place but only very slowly and it took weeks to go to completion whereas, at temperatures above 50°, while the speed of the reaction was greatly increased, the yield of resinous products was quite considerable and the composition of the main product was by no means constant. The optimum temperature as regards constancy of product and speed of reaction was found to be about 40° and all the later oxidations were performed at this temperature.

The first change to be noticed in the reaction mixture was in the upper solid layer which was converted to the liquid state with accompanying evolution of carbon dioxide. When the mixture had become homogeneous, the reaction was considered to be complete. This took from 3 to 5 days, the longer time when caoutchouc was the material oxidised, the shorter with

balata, and an intermediate period with gutta.

Isolation of the Oxidation Products.

The reaction mixture was shaken up in a large separating funnel with water, the chloroform layer, containing the oxidation products, separated, and the aqueous layer extracted repeatedly with chloroform. The combined chloroform extracts were freed from traces of acetic acid by washing with dilute sodium carbonate solution. They were then washed with water and dried over anhydrous sodium sulphate. The solvent was removed below 40° under reduced pressure and the product was obtained as a pale yellow glassy solid. It is to be noted here that, wherever it was possible throughout this work, the working temperature was no higher than 40° in order to reduce to a minimum the risk of condensation or resinification of the products. The above-mentioned solid product was dissolved in alcohol and the solution decanted from any unattacked hydrocarbon . The solvent was removed under reduced pressure and the product recovered as a very pale yellow amorphous solid. It was dissolved in acetone and precipitated as a fine white precipitate by pouring, drop by drop, into a mechanically stirred solution of sodium chloride. The salt solution found to give the most workable product was one in which a saturated solution of common salt was diluted with an equal quantity of water.

Properties of the Oxidation Products.

The three oxidation products from caoutchouc, gutta, and balata were indistinguishable in appearance and in their behaviour towards solvents and various reagents. All three were odourless and colourless amorphous solids. They were insoluble in water, petroleum ether, and carbon tetrachloride and carbon disulphide, sparingly soluble in benzene and in ether, and very soluble in methyl and ethyl alcohols, acetone, chloroform, ethyl acetate, acetic acid and pyridine. None of the products reacted with dilute sodium carbonate solution but all were resinified when kept for a long time in contact with cold caustic alkalies. Numerous attempts were made to crystallise these products from solutions in the above solvents and from various mixtures of such solvents but all were in vain, and, in every case, all that remained after the solvent had been allowed to evaporate very slowly was a sticky syrupy mass. Alcoholic extracts were tested with Schiff's reagent, Fehling's solution, and with ammoniacal silver oxide without indication of the presence of an aldehydic grouping and, in no case, was a semicarbazone obtained on treatment of an alcoholic extract with semicarbazide acetate, The products were unsaturated to bromine and to dilute alkaline potassium permanganate. They decomposed when distilled in vacuo yielding in each case, a dark oily distillate which was not further examined and when

~~and when~~ burned, they emitted the characteristic smell of burning rubber. The conclusion drawn from these observations was that the products were very closely related to the parent hydrocarbons and were of an alcoholic character.

Specimens were analysed and the following results obtained:-

Caoutchouc.

(a) .1590 gm. gave .3650 gm. CO_2 and .1419 gm. H_2O.

(b) .1499 " " .3457 " " " .1345 " "

Found	C.	H.	O.
(a)	62.61	9.91	27.48
(b)	62.88	9.97	27.15
$C_{50}H_{92}O_{16}$ requires	63.29	9.70	27.00

Gutta-percha.

(a) .1647 gm. gave .3360 gm. CO_2 and .1211 gm. H_2O.

(b) .2191 " " .4441 " " " .1611 " "

Found	C.	H.	O.
(a)	55.64	8.17	36.19
(b)	55.29	8.17	36.54
$C_{50}H_{88}O_{24}$ requires	55.97	8.20	35.83

Balata.

(a) .1415 gm. gave .2989 gm. CO_2 and .1094 gm. H_2O.

(b) .1481 " " .3129 " " " .1137 " "

Found	C.	H.	O.
(a)	57.61	8.59	33.80
(b)	57.61	8.53	33.86
$C_{50}H_{88}O_{20}$ requires	59.52	8.73	31.74

Determinations of the molecular weights were made by measuring the depression of the melting point in a camphor solution after the method of Rast. Menthol also was used as solvent and in this case the concentration of the solution was varied from 10% through 2% to 1%. It was noticed that in the more dilute solutions the values obtained were invariably less than in the more concentrated solution.

Oxidation Product	Camphor Solvent	Menthol		
		1:10	1:50	1:100
Caoutchouc	915	498	223	248
	1010	498	244	248
	952	455	244	248
Gutta-percha	998	1031	583	548
	1020	1026	571	543
	1025		576	552
Balata	989	1009	540	524
	1005	987	533	524
	996	993	533	

The OH-content of each of these alcohols was determined by the method of Tschugaeff and Zerewitinoff recommended in Howben-Weyl's "Methoden" Vol.III, p.32 (2nd edition) and based on the reaction between methylmagnesium iodide and a hydroxy-compound which results in the evolution of methane according to the following equation:-

$$CH_3MgI + R.OH = R.OMgI + CH_4$$

The amount of methane evolved from a known weight of substance is measured and serves for the calculation of the OH-content of the compound.

The alcohol was weighed accurately into the bulb of a perfectly dry decomposition flask containing a small side tube. It was dissolved in 15cc. of pure pyridine, dried and distilled over barium oxide, and, into the side arm, was introduced about 5cc. of a Grignard reagent prepared from amyl-ether, magnesium ribbon, and methyl iodide in the usual way. The decomposition flask was attached to a water-jacketed Lunge nitrometer and the whole apparatus allowed to come to constant temperature. The pressure in the decomposition flask was brought to atmospheric by means of the stop-cock and the burette was then filled with mercury. The Grignard reagent was allowed to mix with the solution of hydroxy-substance and, simultaneously, the

decomposition flask and burette were connected through the stop-cock. The reaction mixture was shaken vigorously as long as the mercury in the burette was sinking and was cooled in a water-jacket when evolution of gas had ceased. An initial contraction in volume was followed by a slow increase and the minimum gas volume was measured. The percentage OH-content was found by using the following formula:-

$$x = \%OH = 0.0764 \frac{V}{S}$$

where V = vol. of methane at N.T.P. (in cc's)

S = weight of substance.

Typical results from such measurements are given in the following table:-

Oxidation Product		Wt.of substance	Vol.of methane at N.T.P.	%OH
Caoutchouc	(a)	0.1456 gm	56.4 cc.	29.59
	(b)	0.1123 gm	42.6 cc.	28.98
Gutta-percha	(a)	0.0941 gm	39.7 cc.	32.23
	(b)	0.1272 gm	53.2 cc.	31.96
Balata	(a)	0.1838 gm	62.1 cc.	25.81
	(b)	0.1682 gm	56.6 cc.	25.71

Derivatives of the Oxidation Products.

(a) Action of p-Nitrobenzoyl Chloride.

A solution of the oxidation product in about 10 times its weight of pyridine was cooled in a freezing mixture, p-Nitro-

benzoyl chloride, the proportion being varied in different preparations, was added very slowly with constant stirring. The almost-solid reaction mixture, after standing for 2-3 days at room temperature, was poured into a large volume of water and the pyridine neutralised with dilute sulphuric acid. The product, which was precipitated as a yellowish-brown pasty mass, was filtered, washed with dilute acid and with water, and dried. It was allowed to stand in contact with dilute sodium carbonate solution until all p-nitrobenzoic acid had been removed, rewashed and dried again. It was a friable substance of an orange colour and seemed to contain a small amount of resinous matter. It was extracted repeatedly with ether and the ether, in turn, was removed under reduced pressure from the extract. The brown viscous syrup which was left was redissolved in ethyl acetate and the product precipitated by the addition of petroleum-ether.

The three products were orange-coloured amorphous solids, insoluble in water, benzene, toluene and petroleum-ether, sparingly soluble in ether, chloroform, and in hot carbon tetrachloride, and very soluble in acetone, methyl and ethyl alcohols, ethyl acetate, and pyridine. They gave the usual qualitative tests for nitrogen and esterification, certainly, had occurred to some extent but the products were entirely unsuited to the characterisation of the original alcohols on

account of being contaminated with resinous matter and giving varying results on quantitative estimation of the nitrogen-content.

(b) Action of Phenylcarbimide.

To a solution of the oxidationproduct, cooled in a freezing mixture, was added very slowly phenylcarbimide, at first sufficient to combine with all the oxygen if present as hydroxyl groups but, later, in reduced amount. On being allowed to stand for several days at the ordinary temperature, the reaction mixture assumed a reddish colour and a solid separated on top of the liquid. The reaction mixture was thrown into water and the chloroform layer separated. The solvent was removed in vacuo leaving a brown glassy solid which was extracted with ether several times in an effort to effect separation from contaminating resins. It was finally taken up with benzene and reprecipitated from solution by addition of petroleum-ether. The dried product was fawn-coloured and friable and gave positive nitrogen tests but still contained a fair proportion of resin and was probably even more unsuited to the purposes of the characterisation of the parent alcohol than the corresponding supposed nitrobenzoate had been.

From the preparations a quantity of a colourless crystalline substance was gathered and identified as diphenyl-urea

having a m.p. of 237-8° after recrystallisation.

(c) Action of Phthalic Anhydride on the Metallic Salts.

Solutions of the alcohols in benzene, in which they were only slightly soluble, were treated with the theoretical amount of metallic potassium or metallic sodium. The reaction, in each case, was extremely slow due probably to the sparing solubility of the solute and resulted finally, in the separation of a brown vitreous mass which was thought to be the potassium or sodium salt mixed with a large amount of resin. Preparations were then attempted in dichlorethylene and in ethylene-dichloride solutions and these were found to be more satisfactory solvents for the purpose. When sodium was the reagent used, the reaction proceeded much more smoothly than with potassium and the sodium salt, mixed however with some resin, was obtained as a faintly yellowish paste. It was treated for a few days at the ordinary temperature with phthalic anhydride and the solution, after pouring into water, extracted thoroughly with benzene. The aqueous layer was extracted repeatedly with chloroform and a brown syrupy mass was obtained when the solvent had been removed under reduced pressure. The product obviously contained a large amount of resin and examination of it was abandoned.

(d) Action of Dimethyl Sulphate.

The sodium salt of the alcohol, suspended in dry benzene, was refluxed for a few hours with dimethyl sulphate. After decomposition of excess of reagent by pouring into water, a benzene extraction of the product was made. Removal of the solvent left a reddish-brown vitreous mass, which was extracted several times with sodium-proof ether in an effort to free it from contaminating resins. However, the final product, which was of a dark-brown colour, still contained a large amount of resinous matter and was not submitted to further examination.

Bromination of the Oxidation Products.

The unsaturation of the hydrogen peroxide oxidation products was determined by measuring the bromine additive capacity according to the method employed by Gladstone and Hibbert in their determinations of the bromine additive capacity of caoutchouc. A dilute solution of the oxidation product in chloroform, cooled in a freezing-mixture, was treated with a known volume (an excess) of a standard solution of bromine in chloroform (about 1% solution), starch-potassium iodide paper being used as external indicator to ensure addition of an excess of bromine. The solutions were well mixed by shaking and allowed to stand for 5 minutes. An excess of a concentrated aqueous potassium iodide solution was added and the mixture again well shaken to ensure complete absorption of the residual bromine. The iodine,

thus liberated, was titrated immediately with standard sodium thiosulphate solution using starch solution as indicator. Later determinations were carried out in the presence of potassium bromate in order to avoid possible error due to substitution.

It was observed that addition of the bromine caused an immediate decrease in the viscosity of the solutions of the oxidation products, due very probably to disaggregation of the original molecule. Isolation of the additive compounds was attempted but found to be impracticable on account of the extremely unstable nature of these substances.

The number of determinations of unsaturations carried through is a large one as it was from such measurements that the course of a reaction was followed. The following results are typical of those obtained for the peroxide oxidation products.

Product	Wt. of Substance	Bromine added	Bromine in excess.	Bromine required.	Bromine. for 100pts.
Caoutchouc.	0.2238gm.	.2354gm.	.0452gm.	.1902gm.	85.00
	0.2609gm.	.2354gm.	.0116gm.	.2238gm.	85.76.
	0.2128gm.	.2354gm.	.0552gm.	.1802gm.	85.70.
Gutta Percha.	.6792gm.	.3798gm.	.0744gm.	.3045gm.	44.83.
	.8721gm.	.4537gm.	.0622gm.	.3915gm.	44.89.
	.6573gm.	.3789gm.	.0845gm.	.2944gm.	44.78.
Balata.	.1791gm.	.2023gm.	.1181gm.	.0842gm.	47.01.
	.1689gm.	.2023gm.	.1232gm.	.0791gm.	46.82.
	.2655gm.	.2023gm.	.0777gm.	.1246gm.	46.93.

It was proposed to check these results by determining the iodine values of the oxidation products but this was found to be impracticable because substitution occurred to a large extent, even when precautions were taken to use no more than the theoretical amount of chlorine in the preparation of Wij's solution.

Action of Chromic Acid on the Oxidation Products.

As it seemed futile to continue these attempts at the preparation of an alcohol derivative of sufficient purity for the purpose of characterisation or purification of the parent alcohol, it was decided to attempt the preparation of an aldehyde or ketone by the oxidation of such alcohol. Chromium trioxide in glacial acetic acid solution was chosen as the oxidising agent because its usual effect is to oxidise an alcohol to the corresponding aldehyde or ketone without further oxidation, provided it is used in no more than the theoretical proportion for such a reaction.

Many preliminary oxidations were carried out before the quantity resulting in the best yield of aldehyde was decided. A considerable quantity of an acid product was obtained in the first preparations in which the amount of reagent used was sufficient to oxidise all of the hydroxyl groups supposed to be present in the alcohol. In later experiments, the proportion of oxidising agent was reduced and a reduction in the yield of acid effected until, finally, an aldehyde

was isolated as the only product of the reaction.

The reaction mixtures were as follows:-

Caoutchouc.	Gutta-Percha and Balata.
10g. Alcohol Ic.	10g. alcohol Ig or Ib.
80cc. glacial acetic acid.	80cc. glacial acetic acid.
1.4g. chromium trioxide.	1.2g. chromium trioxide.
40cc. glacial acetic acid.	40cc. glacial acetic acid.

The alcohol was dissolved in the acid and the solution, to which a few drops of water had been added to prevent solidification of the acid, cooled in a freezing-mixture. The second solution, consisting of chromium trioxide dissolved in glacial acetic acid, was also cooled and added, in very small amounts, to the first. During the earlier oxidations a considerable amount of local oxidation occurred resulting in the production of a small amount of resinous acids. Later, by adding the reagent, drop by drop, to a well-stirred solution of the alcohol, such by-products were entirely eliminated.

The reaction mixture was brought to room temperature and allowed to stand overnight. The mixture was thrown into a large volume of water and solid sodium carbonate, sufficient just to fail to neutralise the acid, was added. A white solid product separated as a result of this operation. When it had settled to the bottom of the vessel the supernatant liquid was poured off and the residue dissolved in ether. The aqueous layer was extracted repeatedly with small amounts of ether and all of the ether solutions combined.

The ethereal solution of the product was washed with water and dried over anhydrous sodium sulphate. Partial removal of the ether yielded a greenish-yellow syrup. Complete removal of the solvent under reduced pressure yielded the product as a colourless glassy solid. It was dissolved in acetone and the acetone solution added drop by drop to a constantly agitated solution of common salt. The final product of which, in the later experiments, an almost quantitative yield was obtained was a colourless amorphous solid.

The caoutchouc, gutta, and balata products were almost identical in properties. They were all colourless amorphous solids, insoluble in water, benzene, and petroleum-ether, sparingly soluble in ether and very soluble in methyl and ethyl alcohols, acetone, chloroform, and acetic acid. None of these solvents, however, was suitable as a crystallising medium. Alcoholic extracts of each gave a mirror with ammoniacal silver oxide, reduced Fehling's solution, and restored the colour to Schiff's reagent. They decomposed when distilled, even under reduced pressure, and burned with the characteristic odour of burning rubber.

An ethereal solution of the aldehyde and a saturated solution of sodium bisulphite were left in contact for some time. After 2-3 weeks, a small quantity of solid matter had

separated and was filtered off. This substance was the bisulphite addition compound of the aldehyde and yielded, on decomposing with a strong sodium carbonate solution, a quantity of the original aldehyde. A further quantity of aldehyde was obtained by thorough extraction of the aqueous layer of the reaction mixture with ether followed by decomposition of the extracted bisulphite compound with strong sodium carbonate solution. This method, however, was by no means suited to the purification of the aldehyde and attention was next directed to the preparation of a semicarbazone.

Preparation of the Semicarbazones of the Aldehydes.

To a solution of the aldehyde in ethyl alcohol was added an excess of semicarbazide hydrochloride and the theoretical quantity of sodium acetate, dissolved in a small quantity of water. On standing for a week, a slight colourless precipitate separated and the solution became darker in colour, assuming a yellowish-brown coloration in place of the original greenish-yellow.

The reaction mixture was poured slowly into a well-stirred saturated salt solution and a bulky white precipitate, easily filtered, was obtained. After filtering, washing, and drying, the product was isolated as a colourless amorphous solid entirely free from aldehydic odour.

This white powder was dissolved in alcohol and reprecipitated by stirring into a salt solution in order to remove excess of semicarbazide acetate. The dried product was then treated with cold methyl alcohol and the solution of semicarbazone separated by filtration from the residue, which proved to be a complex condensation product of the semicarbazide. The filtrate was poured slowly into a salt solution and the resulting precipitate filtered, washed, dried, and treated with a large quantity of ether to remove any unattacked aldehyde. It was again brought into solution and reprecipitated in a stirred salt solution. It was filtered, washed, and dried to a white odourless powder entirely free from original aldehyde.

The caoutchouc, gutta, and balata products were alike in appearance and in solubility. They were colourless, odourless, amorphous solids, insoluble in water, benzene, toluene, ether and carbon tetrachloride, sparingly soluble in chloroform, and very soluble in methyl and ethyl alcohols, acetone, and in ethyl acetate. Attempts to obtain them in a crystalline state met with failure. They all gave the Prussian blue precipitate in the qualitative tests for nitrogen.

Analysis of various specimens gave the following results:-

Caoutchouc.

(a) .1895 gm. gave .4039 gm. CO_2 and .1520 gm. H_2O.

(b) .2038 " " .4332 " " " .1623 " "

(a) .3061 " " 21.05 cc nitrogen at 19°C and 752.2 mm.

(b) .3257 " " 22.50 " " "21.5°C " 754.6 ".

Found	C.	H.	N.
(a)	58.12	8.91	7.86
(b)	57.97	8.85	7.83
$C_{52}H_{94}O_{16}N_6$ requires	58.97	8.88	7.94.

Gutta.

(a) .2327 gm. gave .4492 gm. CO_2 and .1588 gm. H_2O.

(b) .2463 " " .4708 " " " .1703 " "

(a) .2792 " " 17.05 cc. N_2 at 16.5° and 763.3 mm.

(b) .3198 " " 19.60 " " " 18° " 758.4 "

Found	C.	H.	N.
(a)	52.64	7.58	7.15
(b)	52.13	7.68	7.08.
$C_{60}H_{90}O_{26}N_6$ requires	51.40	7.41	6.91

Balata.

(a) .2164 gm. gave .4446 gm. CO_2 and .1556 gm. H_2O.

(b) .2283 " " .4668 " " " .1629 " "

(a) .3007 gm. gave 19.50 cc. N_2 at 14.5° and 743.7 mm.

(b) .2953 " " 19.25 " " " 19° " 749.7 "

Found	C	H.	N.
(a)	56.03	7.99	7.46
(b)	55.76	7.93	7.42
$C_{12}H_{90}O_{20}N_6$ requires	55.81	7.90	7.51.

Action of Nitric Acid on the Aldehydes.

About 2 grams of the aldehyde was left in contact with a solution of 5cc. conc. nitric acid (sp.gr. 1.42) in 15cc. water for four days at the ordinary room temperature. The reaction mixture, which had assumed a reddish colour, was then extracted repeatedly with ether. The solvent was partially removed on the water-bath leaving a yellowish solution which, in turn, yielded a reddish-yellow oil on complete removal of the ether under reduced pressure. The oil was readily dissolved by dilute sodium carbonate to a reddish solution. The alkaline solution was filtered and, on acidification, a pale yellow procipitate was formed. The process of dissolving the product in sodium carbonate and reprecipitating by addition of acid was repeated several times. The acid was obtained in a workable form by dissolving in acetone and stirring into a salt solution.

The three products were fawn-coloured granular solids, insoluble in water, benzene, toluene and petroleum-ether, soluble in ether, methyl and ethyl alcohols, acetone and in dilute sodium carbonate and caustic alkali solutions. These products did not contain nitrogen but, when a more concentrated nitric acid solution was used, the products were dark brown in colour and nitrogen-containing. When the reaction was carried out above room temperature there was obtained a resinous mass, nitrogen-containing, and acidic.

Neutral solutions of the ammonium salts of these acids were treated with silver nitrate, lead acetate, calcium chloride, and barium chloride solutions, and only with silver nitrate was a precipitate obtained. These salts were not very stable and decomposed on exposure to the daylight. Therefore, their preparation and estimation of their silver contents were carried through at night in diffused artificial light.

The results obtained were as follows:-

Caoutchouc.

(a) .7148 gm. substance gave .1697 gm. AgCl. Ag = 17.86%

(b) .6347 " " " .1491 " " Ag = 17.68%

Gutta.

(a) .8105 gm. substance gave .1758 gm. AgCl. Ag = 16.32%

(b) .7464 " " " .1613 " " Ag = 16.27%

Palata.

(a) .6276 gm. substance gave .1420 gm. AgCl. Ag = 17.02%

(b) .8053 " " " .1813 " " Ag = 16.94%

Action of Acetic Anhydride upon Perhydrol Oxidation Products.

The original oxidation products having been characterised as alcohols, the preparation of the acetates was attempted. This was effected by treatment of the oxidation product with acetic anhydride in presence of fused sodium acetate. It was observed that the product varied with the time of exposure of the alcohol to the reagent. This was investigated and it was found that a constant product was obtained when the reaction was carried out at 30^0 over a period of 3 hours. The acetyl derivative was precipitated as a yellowish paste when the reaction mixture was thrown into water. It was redissolved in acetone, filtered, and reprecipitated by stirring into a salt solution, the whole operation being repeated several times.

Again there was little difference between the three products. They were colourless, odourless amorphous solids, insoluble in water, benzene, toluene, carbon tetrachloride and petroleum-ether and soluble in ether, methyl and ethyl alcohols, chloroform, acetone, ethyl acetate and pyridine. Specimens submitted to ultimate analysis gave the following results:-

Caoutchouc.

(a) .2234 gm. gave .5613 gm. CO_2 and .1760 gm. H_2O

(b) .1977 " " .4984 " " " .1504 " "

Found	C.	H.	O.
(a)	68.52	8.75	22.73
(b)	68.74	8.45	22.81
$C_{58}H_{88}O_{14}$ requires	69.04	8.73	22.22

Gutta.

(a) .1558 gm. gave .3506 gm. CO_2 and .0986 gm. H_2O.

(b) .2381 " " .5316 " " " .1516 " "

Found	C.	H.	O.
(a)	61.38	7.03	31.59
(b)	60.88	7.07	32.05
$C_{66}H_{92}O_{26}$ requires	60.92	7.08	32.01

Balata.

(a) .1672 gm. gave .3790 gm. CO_2 and .1106 gm. H_2O.

(b) .1705 " " .3874 " " " .1137 " "

Found	C.	H.	O.
(a)	61.81	7.35	30.84
(b)	61.98	7.41	30.61.
$C_{66}H_{96}O_{24}$ requires	62.26	7.55	30.19.

Determination of the molecular weights by the Rast method gave the following results:-

Acetate	Camphor Solvent	Menthol.		
		1:10	1:50	1:100
Caoutchouc	542	512	268	256
	530	524	280	264
	550	532	268	260
Gutta-percha	643	632	350	337
	636	629	346	328
	638	637	341	
Balata	658	627	335	324
	663	621	329	336
	671	627	341	332

A rough estimate of the amount of acetic anhydride taken up during acetylation was made by placing a weighed quantity (about 2gms) of the oxidation product into a conical flask, adding a measured volume of acid-free acetic anhydride and some fused sodium acetate. After refluxing for 3 hours at 30°, the excess of anhydride was decomposed by addition of water and the acid formed estimated, after separation from the acetate by filtration, by titration with standard caustic alkali solution. By titration of a known volume of acetic anhydride all the figures necessary for the calculation of the acetic anhydride absorbed were obtained. The results were as follows:-

Product	Wt.of Product	Acetic Anhydride absorbed	Wt.absorbed by 100g prod.
Caoutchouc	1.9370 gm	.4013 gm	20.71 gm
Gutta percha	2.1273 gm	.7775 gm	36.56 gm
Balata	1.9907 gm	.6972 gm	35.01 gm

Later, the acetate was submitted to analysis by the Perkin method. A weighed amount was treated in a distillation apparatus with a mixture of alcohol and conc.sulphuric acid. The acetic acid, produced by hydrolysis of the ethyl acetate formed after the decomposition of the original acetate, was distilled off into a receiver containing a known amount of standard alcoholic caustic potash. The excess potash was titrated with standard sulphuric acid and, from the quantity of acetic acid formed, the acetyl content of the acetate was calculated giving the following results.

Acetate	Wt.of substance	KOH required to neutralise acetic acid	Equiv.wt. of CH_3CO grouping	$\%CH_3CO$
Caoutchouc	0.7637 gm	0.1949 gm	0.1496 gm	19.60
	1.1629 gm	0.2863 gm	0.2199 gm	18.91
Gutta percha	0.9364 gm	0.3161 gm	0.2428 gm	25.92
	0.9822 gm	0.3241 gm	0.2488 gm	25.34
Balata	1.0747 gm	0.3699 gm	0.2841 gm	26.42.
	0.8212 gm	0.2818 gm	0.2164 gm	26.35

Bromination of the acetates by the usual method gave the following results:-

Product	substance	Bromine added	bromine	Bromine required	Bromine. for 100pts
Caoutchouc	.2112 gm.	.2901 gm	.1532 gm	.1369 gm	64.82 gm
	.1914 gm	.2901 gm	.1663 gm	.1238 gm	64.69
	.3692 gm	.2901 gm	.0493 gm	.2408 gm	65.22
Gutta percha	.3160 gm	.2161 gm	.1378 gm	.0783 gm	24.78
	.3853 gm	.2161 gm	.1204 gm	.0957 gm	24.84
	.4591 gm	.2161 gm	.1022 gm	.1139 gm	24.80
Balata	.6569 gm	.2415 gm	.0749 gm	.1666 gm	25.36
	.6262 gm	.2415 gm	.0823 gm	.1592 gm	25.43
	.7707 gm	.3220 gm	.1269 gm	.1951 gm	25.31

Hydrolysis of the acetates was brought about by heating for several hours at 30° with baryta solution. The alcohol thus produced was purified by repeated fractional precipitations from ethyl acetate solution by means of ether in which solvent the alcohol was less soluble than the corresponding acetate. The products were colourless and amorphous and were submitted to ultimate analyses and the bromine additive capacities and hydroxyl contents were determined. The values obtained are given in the following tables:-

Caoutchouc.

(a) .1623 gm. gave .4215 gm. CO_2 and .1396 gm. H_2O

(b) .1791 " " .4677 " " " .1505 " "

Found	C.	H.	O.
(a)	70.82	9.56	19.62
(b)	71.22	9.34	19.44
$C_{50}H_{80}O_{10}$ requires	71.42	9.52	19.06

Gutta.

(a) .2052 gm gave .4574 gm. CO_2 and .1389 gm. H_2O

(b) .2163 " " .4801 " " " .1458 " "

Found	C.	H.	O.
(a)	60.78	7.52	31.70
(b)	61.30	7.58	31.12
$C_{50}H_{74}O_{18}$ requires	62.24	7.88	29.88

Balata.

(a) .1439 gm. gave .3349 gm. CO_2 and .1084 gm. H_2O

(b) .1513 " " .3565 " " " .1145 " "

Found	C.	H.	O.
(a)	63.48	8.37	28.15
(b)	64.25	8.41	27.34
$C_{50}H_{80}O_{16}$ requires	64.10	8.54	27.36

Product	Wt. of substance	Bromine added	bromine	Bromine required	Bromine for 100pts
Caoutchouc	.2934 gm	.3210 gm	.0943 gm	.2267 gm	77.27 gm
	.2470 gm	.2407 gm	.0519 gm	.1888 gm	76.45 gm
	.2506 gm	.3210 gm	.1287 gm	.1923 gm	76.76 gm
Gutta-percha	.3334 gm	.1986 gm	.0941 gm	.1045 gm	31.34 gm
	.2646 gm	.1986 gm	.1155 gm	.0833 gm	31.48 gm
	.4110 gm	.2185 gm	.0898 gm	.1287 gm	31.32 gm
Balata	.5432 gm	.2328 gm	.0501 gm	.1827 gm	33.62 gm
	.7877 gm	.3492 gm	.0848 gm	.2644 gm	33.57 gm
	.6009 gm	.3492 gm	.1477 gm	.2015 gm	33.54 gm

Alcohol	Wt. of substance	Volume of CH_4 at N.T.P.	%OH.
Caoutchouc	.2596 gm.	28.3 cc.	8.33
	.3356 gm.	37.6 cc.	8.56
Gutta percha	.2335 gm.	40.8 cc.	13.36
	.1736 gm.	29.5 cc.	12.98
	.2002 gm.	34.2 cc.	13.05
Balata	.2842 gm.	52.7 cc.	14.17
	.2380 gm.	44.5 cc.	14.29

Oxidation of the alcohols, thus produced, was effected by means of chromium trioxide and glacial acetic acid as before. The three products of the oxidation were very similar. They were colourless amorphous solids, insoluble in water, benzene and petroleum-ether, sparingly soluble in ether, and very soluble in alcohol, acetone, chloroform and acetic acid.

They all gave the usual tests for an aldehydic grouping with Fehling's solution, ammoniacal silver oxide and Schiff's reagent. From alcoholic extracts semicarbazones were prepared in the usual way. They were amorphous solids, colourless, and without odour. They were insoluble in water, ether, and the hydrocarbon solvents and were very soluble in alcohol and acetone. The usual qualitative test for nitrogen produced positive results. Quantitative estimation of the nitrogen content was carried out by the Kjeldahl method. The results, obtained from such determinations, are given below, together with those obtained from determinations of the carbon and hydrogen contents.

Caoutchouc.

(a) .1932 gm. substance gave .4593 gm. CO_2 and .1516 gm. H_2O

(b) .2175 " " " .5182 " " " .1698 " "

(a) .4808 gm. substance gave .0514 gm. NH_3

(b) .4371 " " " .0467 " "

Found	C.	H.	N.
(a)	64.83	8.72	8.81
(b)	64.97	8.67	8.80
$C_{35}H_{82}O_{10}N_6$ requires	65.68	8.63	8.84

Gutta.

(a).2136 gm. substance gave .4578 gm. CO_2 and .1361 gm H_2O

(b).2184 " " " .4698 " " " .1406 gm "

(a).5032 " " " .0473 " NH_3

(b).4783 " " " .0448 " "

Found.	C.	H.	N.
(a)	58.45	7.08	7.74.
(b)	58.62	7.15	7.72
$C_{78}O_{18}N_6$ requires	58.10	7.26	7.82.

Balata.

(a).1876 gm. substance gave .4143 gm. CO_2 and .1308 gm. H_2O

(b).2093 " " " .4601 " " " .1446 " "

(a).4273 " " " .0414 " NH_3 "

(b).4815 " " " .0464 " "

Found.	C.	H.	N.
(a)	60.23	7.74	7.98
(b)	59.96	7.68	7.94
$C_{82}O_{16}N_6$ requires	59.65	7.83	8.03.

The further oxidation of this aldehyde to an acid could not be effected, as it was in the previous case, by means of nitric acid. The product from this reaction was not acidic in character and contained a fair proportion of

nitrogen. However, an acid product was obtained by drawing a current of air through an alcoholic solution of the aldehyde kept at 40°. A reddish solution was obtained after a fortnight's heating. The solvent was removed, under reduced pressure, leaving a reddish syrup which was to a large extent soluble in dilute sodium carbonate solution. Acidification of the alkaline solution resulted in the formation of a brown gelatinous precipitate. Several times it was dissolved in sodium carbonate solution and reprecipitated by addition of acid. After filtering, washing, and drying, the product was obtained as a brown friable solid.

The three acids were insoluble in water, benzene, toluene, and petroleum——ether, soluble in ether, methyl and ethyl alcohols, acetone and in dilute sodium carbonate and caustic alkali solutions. Neutral solutions of the ammonium salts gave precipitates with silver nitrate and lead acetate solutions, but not with calcium chloride or barium chloride solution, The silver salts were not very suitable for analytical purposes, varying results being obtained for silver content, even when the determinations were made in diffused artificial light. Analysis of the lead salts gave the following results:-

Caoutchouc.

(a).5134 gm. gave .1427 gm. $PbSO_4$ Pb = 19.00%

(b).6142 " " .1692 " " Pb = 18.83%

Gutta.

(a).7252 gm. gave .1822 gm. $PbSO_4$ Pb = 17.17%

(b).6689 " " .1676 " " Pb = 17.12%

Balata.

(a).6421 gm. gave .1652 gm. $PbSO_4$. Pb = 17.58%

(b).6218 " " .1593 " " Pb = 17.50%

Action of Hydrogen Peroxide on the Acetates.

The method used for this oxidation was the same as that employed in the oxidation of the hydrocarbons. Since the acetates were soluble in glacial acetic acid, the use of chloroform as solvent was rendered unnecessary. Otherwise, the oxidation was identical with the previous one and the method of isolating the products was also the same, chloroform being used for their extraction.

These new products were purified by fractional precipitations from solution in alcohol by means of ether, the original acetate being more soluble in the latter than was its corresponding hydrogen peroxide oxidation product.

The products were colourless amorphous solids insoluble in water, benzene, toluene, carbon tetrachloride, and in petroleum-ether, sparingly soluble in ether, and very soluble in methyl and ethyl alcohols, acetone, chloroform, and in ethyl acetate. On slow spontaneous evaporation of the

solvent, from solutions in the above solvents or mixtures of these solvents, all that remained was a syrupy residue. Dilute sodium carbonate did not dissolve these products and dilute caustic alkali caused resinification of them when they were kept for a time in contact with it. Tests for aldehydic groupings with ammoniacal silver oxide, Fehling's solution, and Schiff's reagent were negative and treatment of alcoholic extracts with semicarbazide acetate did not yield any semicarbazone. The products were saturated towards bromine and did not decolourise dilute alkaline permanganate solutions. They could not be distilled without decomposition but when burned they emitted only a trace of the usual smell of burning rubber. From these observations it seemed that the products were alcoholic in nature. In addition to free hydroxyl groups they contained also acetate groupings from the parent acetates. Specimens were analysed as follows:-

Caoutchouc.

(a).2073 gm. gave .4106 gm. CO_2 and .1099 gm.H_2O

(b).2164 " " .4303 " " " .1149 gm H_2O

Found.	C	H	O
(a)	54.01	5.89	40.10
(b)	54.23	5.90	39.87
$C_{58}H_{76}O_{32}$ requires	54.21	5.92	39.87

Gutta.

(a).2075 gm. gave .4134 gm. CO_2 and .1069 gm. H_2O

(b).2063 " " .4093 " " " .1047 " "

Found	C	H	O
(a)	54.33	5.72	39.95
(b)	54.81	5.71	39.48
$H_{84}O_{36}$ requires	54.55	5.79	39.66

Balata.

(a).1986 gm. gave .3976 gm. CO_2 and .1026 gm H_2O

(b).2428 " " .4840 " " " .1250 " "

Found	C	H	O
(a)	54.61	5.74	39.65
(b)	54.37	5.72	39.91
$H_{84}O_{36}$ requires	54.55	5.79	39.66.

The acetyl contents, as determined by the Perkin method, were found to be as follows:-

Product	Wt. of Substance	KOH regd.to neut.acetic acid	Equiv.Wt. of CH_3CO.	% CH_3CO.
outchouc	1.0377gm.	0.2194gm.	0.1685gm.	16.24
	0.8952gm.	0.1849gm.	0.1420gm.	15.86.
tta-Percha	0.9294gm.	0.2785gm.	0.2138gm.	23.01.
	0.9525gm.	0.2856gm.	0.2178gm.	22.87.
lata.	1.0378gm.	0.3103gm.	0.2383gm.	22.96.
	1.1527gm.	0.3416gm.	0.2625gm.	22.76.

Estimation of the hydroxy-contents by the method of Tschugaeff and Zerewitinoff gave the following values:-

Product	Wt. of Substance.	Vol of CH_4 at N.T.P.	% OH.
Caoutchouc	.1976gm.	27.6c.c.	10.67
	.2745gm.	38.5c.c.	10.72
Gutta-Percha	.2752gm.	16.1c.c.	4.47
	.3845gm.	22.8c.c.	4.55
Balata	.4005gm.	25.7c.c.	4.52
	.4459gm.	26.2c.c.	4.49

These acetates were treated for a few hours at 40° with baryta solution. Extraction and precipitation of the products of hydrolysis yielded substances differing only slightly from the parent acetates. In appearance and in behaviour towards solvents, bromine and potassium permanganate, they were identical. They were alcoholic in character but no suitably pure derivative could be prepared from them. They were treated with chromium trioxide in glacial acetic acid in the manner previously described, but no trace of an aldehydic or ketonic product

was obtained. Treatment with Beckmann's mixture (potassium dichromate and conc. sulphuric acid) resulted in the production of a body of high molecular weight, devoid of reducing or acid properties, together with a trace of an acid substance of a resinous nature. Analyses gave the following results:-

Caoutchouc.

(a) .1998 gm. gave .3906 gm. CO_2 and .1112 gm. H_2O

(b) .2059 gm. " .4024 " " " .1126 " "

Found	C	H	O
(a)	53.31	6.18	40.51
(b)	53.28	6.07	40.65
$C_{50}H_{68}O_{28}$ requires	53.76	6.09	40.14

Gutta.

(a) .2238gm. gave .4375 gm. CO_2 and .1225 gm. H_2O.

(b) .2125gm. " .4102 " " " .1170 " "

Found	C	H	O
(a)	53.32	6.08	40.60
(b)	52.65	6.12	41.23
$C_{68}O_{28}$ requires	53.76	6.09	40.14

Balata.

(a) .2243 gm. gave .4427 gm. CO_2 and .1213 gm. H_2O

(b) .2312 " " .4519 " " " .1243 " "

Found	C	H	O
(a)	53.83	6.01	40.16
(b)	53.31	5.97	39.72
$H_{68}O_{28}$ requires	53.76	6.09	40.14.

The following M.W. values were obtained by the Rast Method.

Product	Camphor as Solvent.	Menthol.		
		1:10	1:50	1:100
Caoutchouc	540 539 549	570 592 570	263 254 251	275 271 262
Gutta percha.	581 574	579 568 574	263 259 267	272 268 280
Balata	570 563 579	585 578 591	277 281 289	261 261

The OH-contents were found to be as follows:-

Product	Wt. of Substance	Vol of CH_4 at N.T.P.	%OH.
Caoutchouc	(a) .2129gm.	47.3c.c.	16.97
	.1042gm.	24.4c.c.	19.09
	(b) .1842gm.	42.6c.c.	17.67
Gutta-Percha	(a) .1437gm.	34.7c.c.	18.45
	(b) .1704gm.	41.3c.c.	18.52
Balata	(a) .1946gm.	46.2c.c.	18.13
	(b) .2238gm.	52.6c.c.	17.96

Before passing on to the discussion of the results, reported in the preceding pages, it will be helpful to give, in a paragraph, and outline of the main observations made during the researches. By the hydrogen peroxide oxidation of the hydrocarbons, caoutchouc, gutta, and balata, products of an alcoholic character were produced. These products have been termed, respectively; alcohols Ic, Ig, and Ib. Further oxidation with chromic acid resulted in the formation of aldehydes Ic, Ig, Ib, and these, in turn yielded acids Ic, Ig, and Ib on oxidation with nitric

acid. By treatment of the above-mentioned alcohols Ic, Ig, and Ib with acetic anthydride there was obtained a corresponding series of acetates, namely acetates Ic, Ig, and Ib which yielded, on hydrolysis, alcohols Iac, Iag, and Iab respectively. The latter alcohols were oxidised with chromic acid and gave aldehydes IIc, IIg, and IIb, which, on further oxidation with atmospheric oxygen, yielded acids IIc, IIg, and IIb, By treating acetates Ic, Ig, and Ib with hydrogen peroxide, new compounds, containing both acetyl groups and hydroxyl groups were prepared. These were termed acetates IIc, IIg, and IIb respectively. Hydrolysis of the new acetates was performed and alcohols IIc, IIg, and IIb were isolated. Analytical results, obtained from these last three products were in so close agreement that it was concluded that they were identical, and, accordingly, they have been termed simply alcohol II.

PART III CONCLUSION.

While no product of a crystalline nature has been obtained as a result of this work and no criterion is available to guarantee the absolute purity of any of the products, yet, since there is fairly close agreement between the analyses of different specimens of each of the products, it may fairly safely be assumed that the products are definite individual compounds and not mixtures.

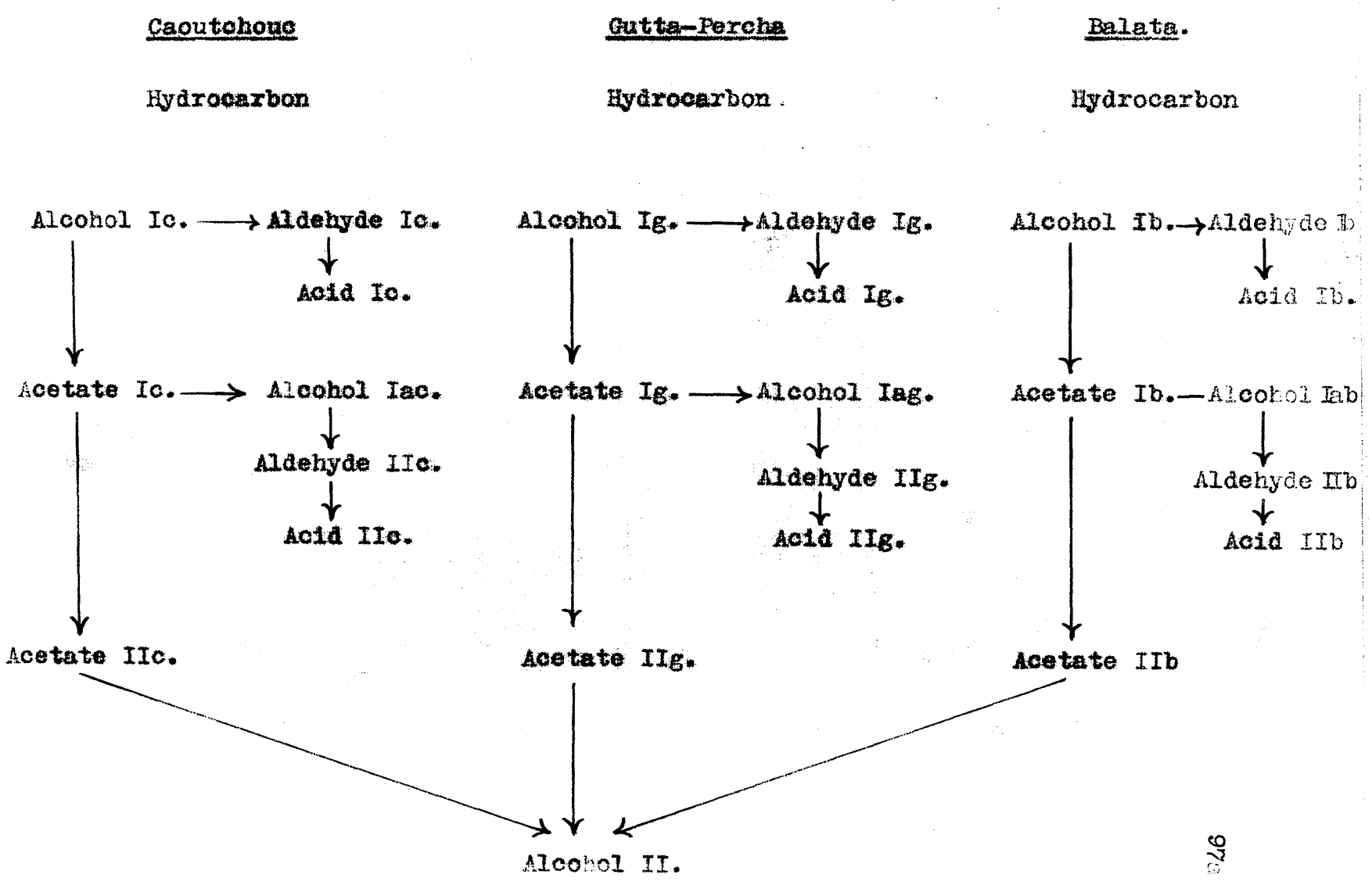
The results generally reveal a very close parallelism in the behaviour towards the reagents used, of the three hydrocarbons, caoutchouc, gutta-percha and balata, and their various derivatives. The only difference shown by the three substances in this work seems to be in the extent of the changes produced and not in the nature of these changes. A superficial examination of the results seems to show that there is a difference, however subtle, between the constitutions of the three compounds and, also, that the relationship existing between gutta-percha and balata is much closer than that existing between either of them and caoutchouc. The differences exhibited by the several products, diminish gradually as we progress through the series until, finally, we reach a point at

which the three products give analytical results so very similar that it has been assumed that they are identical.

The diagram on the following page has been drawn up to show the nature of the various products isolated and the general relationship existing in the series.

Since all of the products were non-crystalline solids, which decomposed on distillation even under reduced pressure, it was almost impossible to obtain a complete separation from resinous materials once these were formed. So all the preparations were carried through under conditions which reduced to a minimum the danger of the formation of such undesirable by-products.

The product of the hydrogen peroxide oxidation of caoutchouc was a colourless amorphous solid approximating to the composition $C_{52}H_{95}O_{17}$. It did not possess acidic or reducing properties and was thought to be an alcohol corresponding to the products obtained from similar treatment of the terpenes. Owing to the colloidal nature of the product and the consequent small depression in the freezing-point of solvents, it was impossible to obtain an accurate determination of its M.W. by the cryoscopic method. So, a M.W. determination by the Rast method using camphor as solvent was attempted. The values obtained, however, were very variable and no great


Caoutchouc
Hydrocarbon
Alcohol Ic.
Aldehyde Ic.
Acid Ic.
Acetate Ic.
Alcohol Iac.
Aldehyde IIc.
Acid IIc.
Acetate IIc.
Gutta-Percha
Hydrocarbon
Alcohol Ig.
Aldehyde Ig.
Acid Ig.
Acetate Ig.
Alcohol Iag.
Aldehyde IIg.
Acid IIg.
Acetate IIg.
Balata.
Hydrocarbon
Alcohol Ib.
Aldehyde Ib
Acid Ib.
Acetate Ib.
Alcohol Iab
Aldehyde IIb
Acid IIb
Acetate IIb
Alcohol II.

reliance could be placed upon them as a means of fixing the actual M.W. because, under the conditions of the determination, the product could quite well undergo polymerisation or depolymerisation. The results were even more unsatisfactory when menthol was the solvent employed. A 10% solution in this solvent gave M.W. values in the region 950-1000 i.e. they were comparable with those given by camphor, but when the concentration was reduced to 2% the value obtained was approximately half of the above i.e. about 500 and when the solution was diluted to 1% there was again reduction of a half in the M.W. value to about 250. While these results were of little value in fixing the actual M.W. of the product under examination, they served to give an idea of the minimum unit on which to base the empirical formula, namely, C_{25} or C_{30}.

Since the product was an alcohol, an attempt was made to prepare its nitrobenzoate but the product isolated from the esterification was not suited to analytical purposes on account of its being contaminated with resinous matter, formed during the reaction. Similarly, attempts at the preparation of a phenylurethane and an acid phthalate in the pure state were unsuccessful and produced even less satisfactory results. Attention was then directed to the

preparation of an aldehyde or a ketone by oxidation of the alcohol.

Treatment of the alcohol with chromic acid resulted in the formation of a body of pronounced aldehydic properties, reducing ammoniacal silver oxide and Fehling's solution, and restoring the colour to Schiff's reagent. When an alcoholic solution was treated with an excess of semicarbazide acetate, a semicarbazone was produced and gave a mean N content of 7.85% . Assuming the derivative to be a monosemicarbazone, its M.W. should be in the region of 530, and that of the parent aldehyde about 470.

An acid was obtained by further oxidation of the above aldehyde by means of dilute nitric acid. A neutral solution of its ammonium salt was treated with silver nitrate and the silver salt precipitated. The mean silver content of this salt was 17.78% representing a M.W. of at least, 608 for the silver salt and corresponding to a M.W. of about 500 for the acid itself, a result in fairly close agreement with the 486 derived from the aldehyde through the semicarbazone. Calculating from the average of these two acid values the M.W. of the corresponding alcohol should be about 480.

The alcohol approximated to the composition $C_{52}H_{95}O_{17}$ so that reduction to a C_{25} basis would give $C_{25}H_{46}O_8$ of

M.W.474 in fair agreement with the minimum M.W. calculated from the above semicarbazone and the silver salt. Since it yielded an aldehyde on oxidation, it must contain a primary alcohol grouping and, therefore, can be written in the form $C_{24}H_{43}O_7CH_2OH$. The aldehyde would then be $C_{24}H_{43}O_7$. CHO and the semicarbazone $C_{25}H_{44}O_8(CN_3H_3)$. The acid would have the formula $C_{24}H_{43}O_7$.COOH and its silver salt $C_{24}H_{43}O_7$.COOAg. The calculated N content of the above semicarbazone is 7.94% and the calculated silver content of the salt, 18.15%. The actual values obtained were 7.85% and 17.78% respectively so that the conclusion reached concerning the partial constitution of the alcohol seemed to be justified.

Now, as some of the oxygen in the alcohol, $C_{25}H_{46}O_8$, might have been present as ether oxygen the OH-content was determined by measuring in a suitable apparatus the volume of methane evolved when the alcohol was treated with $MgCH_3I$. The mean OH-content was 29.28% indicating that eight -OH groups were present in $C_{25}H_{46}O_8$. Thus, the whole of the oxygen was present as -OH groups and the formula was written, therefore, as $C_{25}H_{38}(OH)_8$, one of the OH groups being contained in a $-CH_2OH$ grouping. A monocyclic compound of the above formula should be saturated by the addition of 4 Br atoms equivalent to

76.19% by weight, but it was found that the product added on 85% of bromine. The explanation of this high result might be that either the compound under examination was an open-chain compound or that some secondary reaction such as oxidation had taken place concurrently with the addition of bromine.

Alcohol Ic was treated with acetic anhydride and converted into an acetate (Ic) which was hydrolysed with baryta yielding an alcohol (Iac) of the composition $C_{59}H_{94}O_{12}$. Alcohol Iac was oxidised by means of chromic acid to an aldehyde from which a semicarbazone was prepared. The aldehyde was still further oxidised with atmospheric oxygen to an acid and a lead salt of this acid prepared. The composition of this salt served to fix a basis of calculation for the whole series. The mean lead content was 18.9% which indicated that, if the salt were normal, the acid would be dibasic and of M.W. 1095-207+2=890 a fact which necessitated a change from the C_{25}- to a C_{50}-basis. Alcohol Ic was therefore, written as $C_{50}H_{76}(OH)_{16}$ and was assumed to yield a dialdehyde and then a dibasic acid.

Reduction of $C_{59}H_{94}O_{12}$, alcohol Iac, to a C_{50}-basis gave as the empirical formula $C_{50}H_{80}O_{10}$. The mean OH-content of this alcohol was found to be 8.46% corresponding to 4-OH groups per $C_{50}H_{80}O_{10}$ and the formula was written as

$C_{50}H_{76}O_6(OH)_4$ indicating an unsaturation of 8 or an additive capacity for 76.19% bromine in agreement with the observed addition of 76.8% bromine. Now, since this alcohol yielded on oxidation a dialdehyde it must contain two primary alcohol groups and, therefore may be given the form $C_{48}H_{72}O_6(OH)_2.(CH_2OH)_2$. The aldehyde would then be $C_{48}H_{72}O_6(OH)_2.(CHO)_2$ and its semicarbazone $C_{48}H_{72}O_6(OH)_2.(CHO.CN_3H_3)_2$ of calculated N content 8.84% agreeing closely with the found value 8.80% The acid which would be obtained from such an aldehyde would have the composition $C_{48}H_{74}O_8.(COOH)_2$ and its lead salt would be $C_{48}H_{74}O_8(COO)_2$ Pb of lead content 19.29% in close agreement with the found value 18.9%

Since alcohol Iac $C_{50}H_{76}O_6(OH)_4$ was derived from acetate Ic by hydrolysis, the latter compound should have the structure $C_{50}H_{76}O_6(O,OCCH_3)_4$. Ultimate anlayses agreed fairly well with such a formula, but measurement of the acetyl content by means of the Perkin method gave 19.25%, a result not in too close agreement with the calculated value 17.06% This high figure may have been due to the formation of some volatile acid in the decomposition of the alcohol, product of hydrolysis of the acetate during the distillation of the acetic acid. The measured unsaturation corresponded to an addition of 64.98% bromine and was quite

close to the calculated figure 63.49%. As it was desired to obtain an idea of the general relationship holding over the whole series rather than absolute agreement between the quantitative results and the values calculated from the proposed empirical formulae, the formula for the acetate Ic was left as given above without readjustment to obtain a closer agreement between calculated and found analyses.

Acetate Ic, to which has just been assigned the formula $C_{50}H_{76}O_6(OOCCH_3)_4$, was derived from alcohol Ic, $C_{50}H_{76}(OH)_{16}$ by treatment of the latter with acetic anhydride. It is obvious that it has not been produced by simple acetylation of the OH groups. When the formula of alcohol Ic above is compared with that of alcohol Iac, $C_{50}H_{76}O_6(OH)_4$, (derived from acetate Ic), it is seen that, in the second formula, 12 OH groups of the first have been replaced by 6 O atoms. It would seem, therefore, that acetylation of some of the OH groups in alcohol IC had been accompanied by loss of the elements of water. Such a reaction could take place quite well under the influence of acetic anhydride and could be represented as follows:-

$$C_{50}H_{76}(OH)_{16} - 6H_2O = C_{50}H_{76}O_6(OH)_4.$$

Acetate Ic was still unsaturated and it was subjected to the further oxidising action of hydrogen peroxide. There

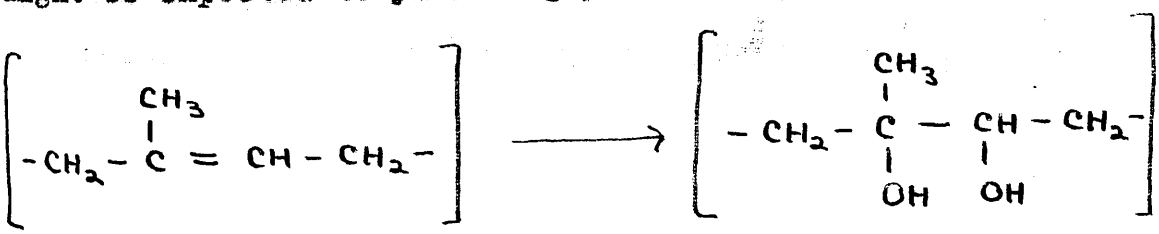
was isolated a new product acetate IIc, containing free OH groups in addition to the CH_3CO-groups of the original acetate Ic and having a composition approximating to $C_{58}H_{76}O_{32}$. Hydrolysis with baryta produced an alcohol (IIc) of the composition $C_{50}H_{68}O_{28}$. When the C/H ratio of alcohol IIc, namely 8.7, is compared with that of alcohol Ic, 6.31, it is evident that there has been a loss of hydrogen between alcohol Ic and alcohol IIc and, since the loss is too great to be accounted for by means of mere loss of the elements of water, it must have occurred between acetate Ic and alcohol IIc. But alcohol IIc was obtained by simple hydrolysis of acetate IIc so that the loss of hydrogen must have taken place in the oxidation of acetate Ic to acetate IIc. This question will be further investigated after the partial constitution of alcohol IIc has been ascertained.

The empirical formula ascribed to alcohol IIfrom ultimate analyses was $C_{50}H_{68}O_{28}$. The mean OH-content was found to be 17.5% corresponding to 12 OH groups per $C_{50}H_{68}O_{28}$ so that the formula was expanded to $C_{50}H_{56}O_{16}(OH)_{12}$. The calculated OH-content of such a compound is 18.27% and, for C_nH_{2n}, such an alcohol should be saturated, in complete accordance with the observations. An acetate, which could yield on hydrolysis an alcohol of the above formula and which would have CH_3CO- and OH-contents approximating to

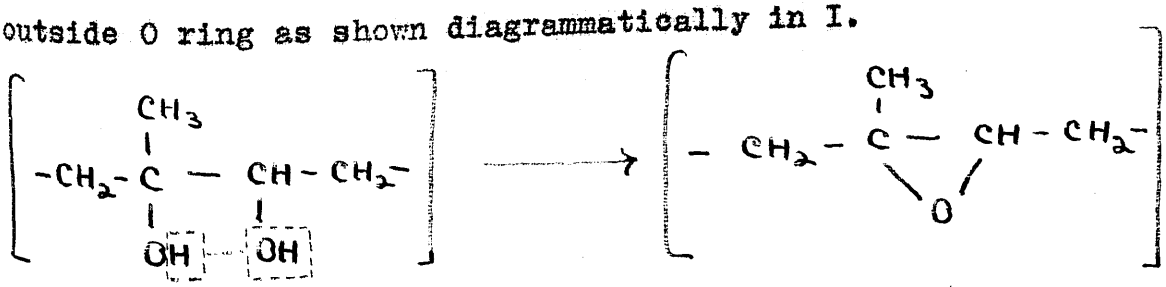
the observed values for acetate IIc, was reckoned to be $C_{50}H_{56}O_{16}(OH)_8(OOCCH_3)_4$. An acetate of this formula would give a calculated CH_3CO-value of 13.39% somewhat lower than that found for acetate II i,e, 16.05%, but it would give an OH-content agreeing very closely with the observed value (calculated 10.59%; found 10.7%). An acetate such as the above would be saturated to bromine and this was confirmed for acetate II. So, acetate II was supposed to have the formula $C_{50}H_{56}O_{16}(OH)_8(OOCCH_3)_4$

We can now consider the mechanism of the oxidation of acetate Ic of formula $C_{50}H_{76}O_6(O.OCCH_3)_4$ to acetate IIc of formula $C_{50}H_{56}O_{16}(OH)_8OOCCH_3)_4$. The net result of the oxidation has been a loss of 20 H atoms and an unsaturation of 8 and a gain of 8 OH groups and 10 O atoms. As would be expected the four acetate groups of I have been retained in II. Since there is no evidence of the presence of $>CO$ or -COOH groups in II, the replacement of hydrogen by oxygen must have been brought about in some way by the elimination of the elements of water following an initial addition of -OH groups. This addition of -OH groups and subsequent dehydration may have occurred in several ways, enumerated below, and it is proposed that a balance has been set up between them with the production of the observed results.

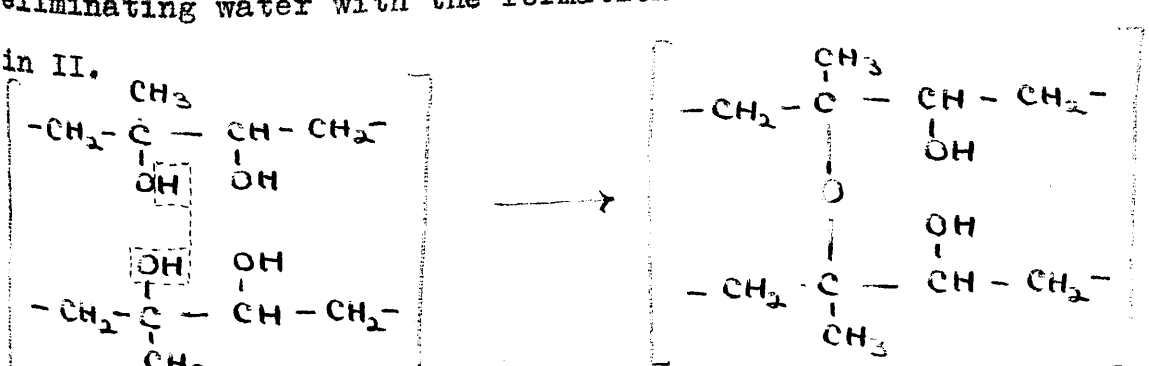
Taking the generally accepted unit of the caoutchouc molecule, it is seen that oxidation with hydrogen peroxide might be expected to yield a glycol as follows:-



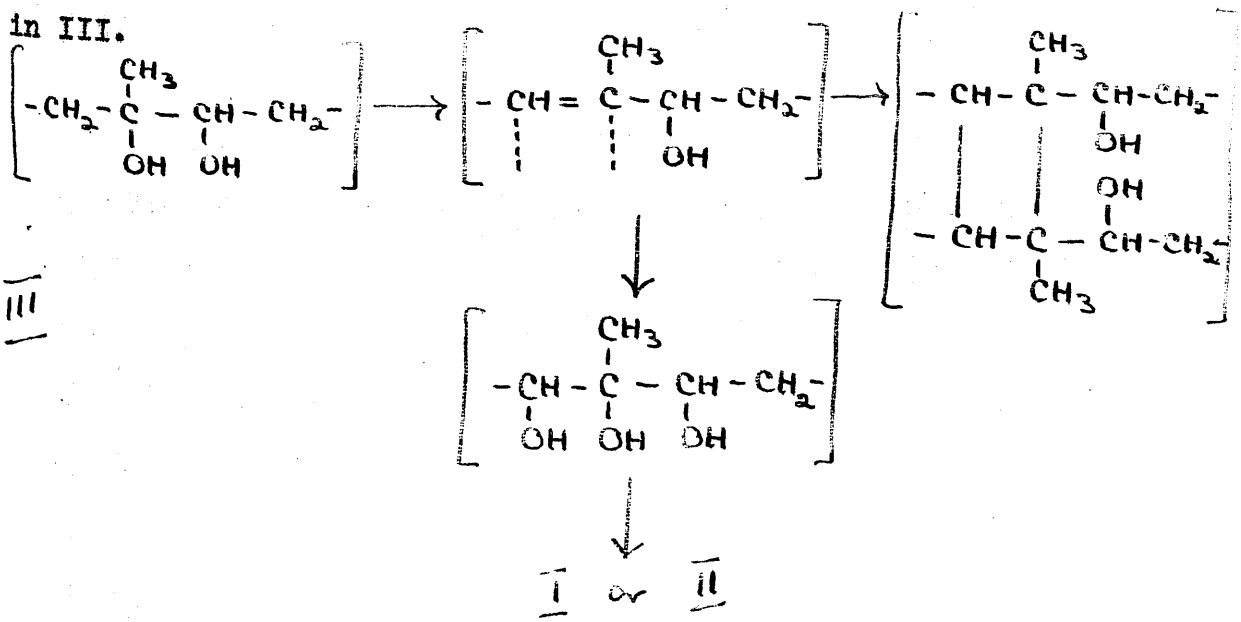
Removal of the elements of water from 2 OH groups attached to adjacent C atoms would result in the formation of an outside O ring as shown diagrammatically in I.



Again, it might be supposed that, in a molecule of the size of the supposed caoutchouc molecule, 2 -OH groups on opposite sides of the molecule might be capable of eliminating water with the formation of an inner ether as in II.



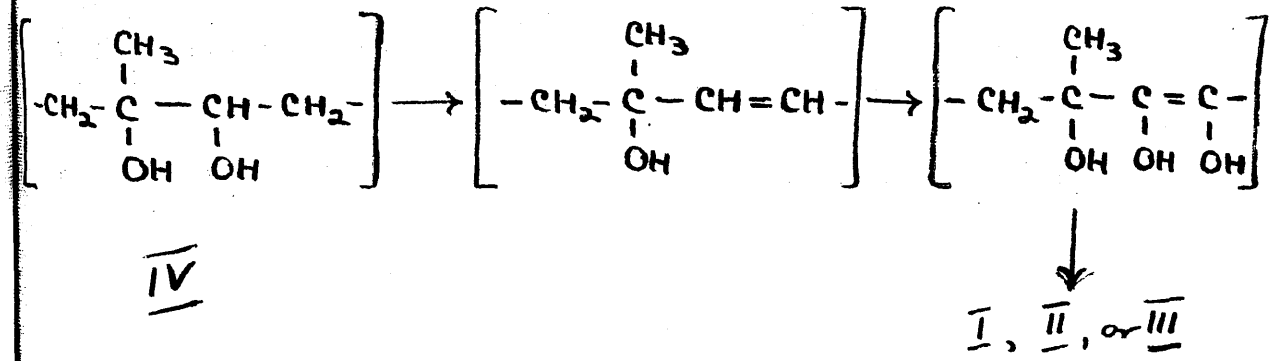
Another possibility is the removal of a tertiary alcohol group with a H atom of the adjacent $-CH_2-$group, with the production of a double bond. In order to restore the compound to its original unsaturation, there might occur a further addition of -OH groups, which might then eliminate water according to I or II or, again, 2 double bonds formed as above, might become mutually saturated by internal ring formation. These possibilities are shown in III.



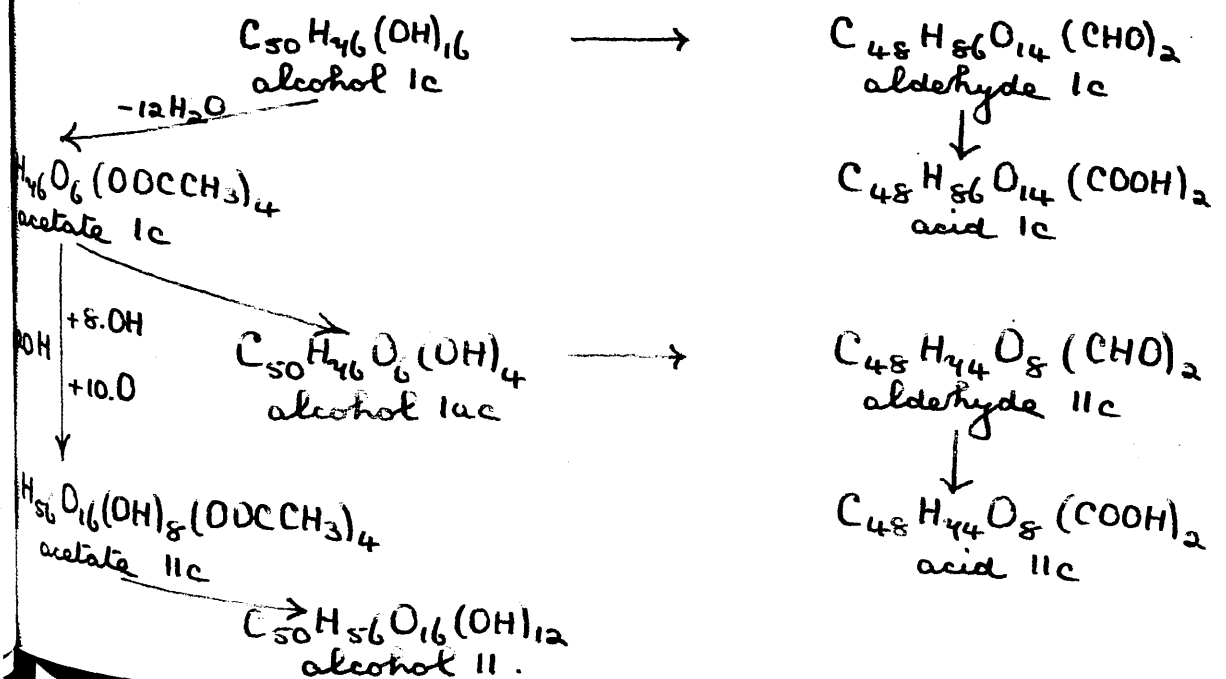
III

Finally, a secondary alcohol group might be removed along with a H atom of the adjacent $-CH_2-$group with the formation of a double bond of the type, -CH=CH- which might become saturated by addition of -OH groups or by internal ring

formation. Also, replacement of the H atoms of such a grouping might occur before such saturation took place. (IV)



It is proposed that the various changes, summarised below, result from reactions such as the above, but, on account of the dimensions of the caoutchouc molecule, no attempt has been made to indicate to what extent each is supposed to take place. The results so far obtained are summarised in the following scheme:-



A similar scheme was worked out for gutta-percha by a process of reasoning the same as that adopted in the interpretation of the results in the caoutchouc series. The empirical formula ascribed to alcohol I in the gutta series was $C_{50}H_{68}O_4(OH)_{20}$ which showed that replacement of hydrogen by means of oxygen had taken place in the oxidation of the hydrocarbon. In this respect the oxidation of gutta-percha differed from that of caoutchouc in which there was only addition of -OH groups. The observed unsaturation as measured by the addition of bromine, 44.85%, was greater than that calculated from the above formula namely 29.84%. A similar observation was made for caoutchouc and the explanations put forward in that case would hold perfectly well in this case also. The mean -OH-content of alcohol Ig was 32.1%, in fair agreement with the calculated value 31.71%. As the alcohol on oxidation gave a dialdehyde, its formula was expanded to $C_{48}H_{64}O_4(OH)_{18}(CH_2OH)_2$ so that the aldehyde was $C_{48}H_{64}O_4(OH)_{18}.(CHO)_2$ yielding a semicarbazone $C_{48}H_{64}O_4(OH)_{18}.(CHO.CN_3H_3)_2$ of calculated N content 6.91% and an acid, $C_{48}H_{64}O_4(OH)_{18}.(COOH)_2$ which would yield a silver salt containing 16.49% silver. The actual values found were 7.11% N and 16.3% Ag.

By treating alcohol Ig.with acetic anhydride a compound,

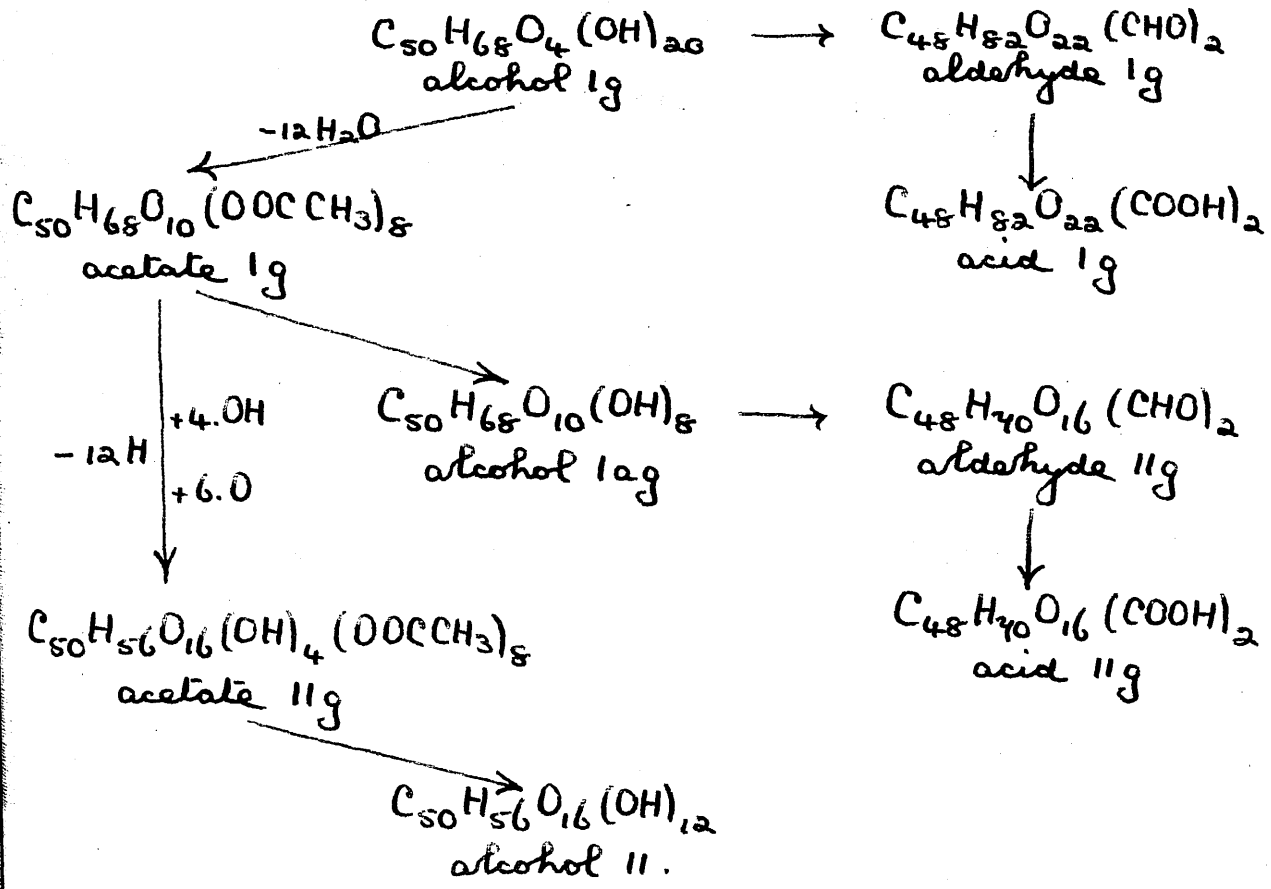
acetate Ig, approximating to $C_{66}H_{92}O_{26}$ was obtained. The mean CH_3CO-content of this substance was 26.46% and corresponded to 8 CH_3CO-groups per $C_{66}H_{92}O_{26}$ so that acetate Ig was given the formula $C_{50}H_{68}O_{10}(OOCCH_3)_8$. Hydrolysis of such an acetate should yield an alcohol of the composition $C_{50}H_{68}O_{10}(OH)_8$ with a -OH-content of 14.1% and an unsaturation equivalent to the addition of 33.19% bromine. Alcohol Iag gave values of 13.13% OH and 31.48% Br and these were considered close enough to permit of the assumption that it possessed the above formula. On account of its oxidation to a dialdehyde it was written more fully in the form $C_{48}H_{64}O_{10}(OH)_6.2CH_2OH$. The aldehyde from this alcohol should have the composition $C_{48}H_{64}O_{10}(OH)_6.2CHO$ and should give a semicarbazone of N content 7.82% and an acid whose lead salt would contain 17.29% lead. Analyses of the semicarbazone gave a mean N content of 7.74% and of the lead salt 17.15% of lead, figures agreeing sufficiently with the calculated values to prove the correctness of the proposed formula for alcohol Iag, namely $C_{50}H_{68}O_{10}(OH)_8$.

Treatment of acetate Ig, $C_{50}H_{68}O_{10}(OOCCH_3)_8$, with perhydrol resulted in the formation of acetate IIg, $C_{66}H_{84}O_{36}$. This product was saturated to bromine and gave a mean acetyl content of 22.94% corresponding to 8 CH_3CO-groups

per $C_{66}H_{84}O_{36}$ and a mean OH-content of 4.5% corresponding to 4 OH-groups for a molecule of the same size. On these grounds, it was assigned the formula $C_{50}H_{56}O_{16}(OH)_4(OOCCH_3)_8$ of calculated CH_3CO-content and OH-content 23.69% and 4.68% respectively. This acetate gave by hydrolysis an alcohol, $C_{50}H_{56}O_{16}(OH)_{12}$, identical in composition with that obtained at the corresponding stage of the caoutchouc series.

Thus, in recapitulation, there was obtained, by the oxidation of gutta-percha, an alcohol, $C_{50}H_{68}O_4(OH)_{20}$ in the formation of which addition of -OH groups has been accompanied by removal of water in such a way that the net result has been an elimination of 12 H atoms and an addition of 20 OH groups and 4 O atoms with the production of an unsaturation of 4. When this alcohol was treated with acetic anhydride, 8 OH groups were acetylated and the equivalent of 12 H_2O removed giving acetate I of the composition $C_{50}H_{68}O_{10}(OOCCH_3)_8$. Acetate Ig was oxidised with perhydrol to acetate IIg, $C_{50}H_{56}O_{16}(OH)_4(OOCCH_3)_8$ formed by addition of OH groups and removal of water in such a way that 12 H atoms were removed, 6 O atoms and 4 OH groups added, and a saturated substance formed. Hydrolysis of acetate IIg gave an alcohol, $C_{50}H_{56}O_{16}(OH)_{12}$ of composition the same as that of alcohol IIg in the caoutchouc series.

These changes have been summarised in the following scheme.



Analogous transformations were shown to occur in the balata series. Alcohol Ib was given the formula $C_{50}H_{72}O_4(OH)_{16}$. Its OH-content and unsaturation were calculated to be 26.98% and 31.74% respectively while the results obtained by determination were 25.77% and 46.94%. As in the two previous series the bromine absorption of alcohol I is here much higher than the calculated value. The aldehyde from alcohol I was given the formula $C_{48}H_{82}O_{18}.(CHO)_2$ and its semicarbazone $C_{48}H_{82}O_{18}(CHO.CN_3H_3)_2$ so that the latter should have a N content of 7.51%. The figure obtained from

Kjeldshl estimation was 7.44%. The silver salt of the acid derived from alcohol Ib was calculated to contain 17.28% and the actual silver content obtained by estimation was 16.99%. From the close agreement of these calculated and observed values the formula which was given originally to alcohol Ib seemed to be fully justified.

Alcohol Ib was treated with acetic anhydride and converted into acetate Ib of composition $C_{66}H_{96}O_{24}$. The latter's acetyl content of 26.39% indicated the presence of 8 CH_3CO groups per $C_{66}H_{96}O_{24}$ so that the empirical formula was $C_{50}H_{72}O_8(OOCCH_3)_8$ of calculated unsaturation equivalent to the addition of 25.16% bromine in agreement with the observed addition of 25.37%. The acetyl content calculated from the above formula was 27.2%. Once more, acetylation has been accompanied by removal of water, this time to the extent of 8 H_2O mols. per C_{50}. Hydrolysis of acetate Ib yielded alcohol Iab, $C_{50}H_{80}O_{16}$, having a OH-content of 14.23% and an unsaturation equivalent to 33.75% bromine in fair agreement with the OH-content of 14.52% and unsaturation of 34.18% calculated from $C_{50}H_{72}O_8(OH)_8$. By oxidation of alcohol Iab, there was prepared aldehyde IIb whose semicarbazone contained 7.96% nitrogen. It was represented by $C_{48}H_{74}O_{14}\cdot(CHO)_2$, the semicarbazone of which should have a N-content of 8.03%. Oxidation of aldehyde IIb

produced an acid which yielded a lead salt containing 17.54% lead agreeing closely with the calculated lead content of $C_{48}H_{74}O_{14}(COO)_2Pb$, namely 17.7% and proving the correctness of the formula assigned to acetate Ib, $C_{50}H_{72}O_8(OOCCH_3)_8$.

Oxidation of acetate Ib produced the saturated acetate IIb of composition $C_{66}H_{84}O_{36}$ and of acetyl and OH contents 22.86% and 4.51% respectively, corresponding to the possession of 8 CH_3CO- and 4 OH-groups per $C_{66}H_{84}O_{36}$. The formula, therefore, was $C_{50}H_{56}O_{16}(OH)_4(OOCCH_3)_8$ and identical with that given to the corresponding derivative in the gutta-percha series. Hydrolysis of acetate IIb yielded alcohol IIb which was saturated and had a OH-content of 18.05, in close agreement with that required for an alcohol of the same formula, as that given to alcohol II in each of the two series previously described.

The changes as detailed above taking place in the balata series are outlined in the following scheme:

$C_{50}H_{42}O_4(OH)_{16}$ alcohol 1b → $C_{48}H_{82}O_{18}(CHO)_2$ aldehyde 1b

$C_{48}H_{82}O_{18}(COOH)_2$ acid 1b

$C_{50}H_{42}O_8(OOCCH_3)_8$ acetate 1b

$C_{50}H_{42}O_8(OH)_8$ alcohol 1ab → $C_{48}H_{44}O_{14}(CHO)_2$ aldehyde 11b

$C_{48}H_{44}O_{14}(COOH)_2$ acid 11b

$-16H$ $+4.OH$ $+8.O$

$C_{50}H_{56}O_{16}(OH)_4(OOCCH_3)_8$ acetate 11b

$C_{50}H_{56}O_{16}(OH)_{12}$ alcohol 11

In order to obtain an idea of the general relationship existing between the three series the scheme given below has been drawn out.

Caoutchouc.	Gutta-percha.	Balata.
$C_{50}H_{46}(OH)_{16}$ alcohol 1c	$C_{50}H_{68}O_4(OH)_{20}$ alcohol 1g	$C_{50}H_{42}O_4(OH)_{16}$ alcohol 1b
$C_{50}H_{46}O_6(OOCCH_3)_4$ acetate 1c	$C_{50}H_{68}O_{10}(OOCCH_3)_8$ acetate 1g	$C_{50}H_{42}O_8(OOCCH_3)_8$ acetate 1b
$C_{50}H_{56}O_{16}(OH)_8(OOCCH_3)_4$ acetate 11c	$C_{50}H_{56}O_{16}(OH)_4(OOCCH_3)_8$ acetate 11gb	

$C_{50}H_{56}O_{16}(OH)_{12}$ alcohol 11.

The empirical formulae which have been assigned to the various products in the above scheme show that the nature of the action of the various reagents on the three hydrocarbons, caoutchouc, gutta-percha, and balata, is the same but that there is a difference in the extent of the reaction in the three cases. It has been proposed already that the observed changes have been brought about by the addition of -OH groups, by means of hydrogen peroxide, by direct addition to the double bonds and by replacement of H atoms, followed by removal of the elements of water under the influence of acetic anhydride. The formulae given above show also that whatever difference exists between the constitutions of the three hydrocarbons, that between gutta-percha and balata is less than that between either of these and caoutchouc. They all, however, come down finally, to the same unit.

While the results have been calculated on a C_{50} basis it is not suggested that this corresponds to the size of the caoutchouc, gutta-percha, or balata molecules. It is suggested, on the other hand, from the character of the various products isolated, that the molecule of each is very much larger than, and some multiple of, $C_{50}H_{80}$.

----------oOo----------

REFERENCES.

1. Harries; Untersuchungen über die Kautschukarten p.7. (1919.)
2. Pummerer and Burkhard; Ber., 1922, 55, 3458.
3. Pummerer and Koch; Ann., 1924, 438, 295.
4. Caspari; J. Soc. Chem. Ind., 1913, 32, 1041.
5. Pummerer and Pahl; Ber., 1927, 60, 2152.
6. Whitby; Ind. Rubb. Journ., 1913, 45, 1043
7. Harries; Ann., 1914, 406, 198.
8. Hinrichsen and Kindscher; Ber., 1909, 42, 4329.
9. Pummerer Nielson & Stundl; Ber., 1927, 60, 2167.
10. Katz; Chem. Ztg., 1925, 49, 353.
11. Hauser & Mark; Koll-chem. Beihefte, 1926, 22, 23; 23, 64.
12. Clark; Ind. Eng. Chem., 1926, 18, 1131
    1929, 21, 128.
13. Bary and Hauser; Rubber Age. 1928, 23, 685.
14. Barnard; "Dictionary of Arts" Dr. Ure 1853, page 358
15. Beale and Pnderby; L'Institut. 1834, page 290
16. Himly; London & Edinburgh Phil. Mag., 1836, vol IX p.322 (3rd. series)
17. Gregory; London & Edinburgh Phil. Mag. 1836, Vol IX p.479 (3rd. series)

18. Bouchardat; Journ.de Pharm., 1837, 23, 457.
19. Williams; Proc.Roy.Soc., 1860, 10, 516.
20. Wallach; Ann.der.Chemie, 1885, 227, 292-6
21. Bouchardat & Lafont; Ann.Chem.Phys., 1886, pp.507, 534.
22. Tilden; Chem.News. 1882, 46, 220.
23. Ipatieff and Wittorf; J.Prakt Chem., 1897, 55(2), 4
24. Gadziatzky; Journ of Russ.Phys.Chem.Soc. 20, 706.
25. Euler; Ber., 1897, 30, 1989.
26. Harries Ber., 1902, 35, 2158.
27. Staudinger & Fritschi; Helv.Chim.Acta. 1922, 5, 785.
28. Staudinger & Geiger; Helv.Chim.Acta. 1926, 9, 549.
29. Midgley & Henne; J.Amer.Chem.Soc., 1929, 51, 1215.
30. Bouchardat; Comptes Rend., 1875, 80, 1446.
31. Bouchardat; Comptes Rend., 1879, 89, 1117.
32. Tilden; Chem.News., 1884, 45, 410.
33. Wallach; Ann.der Chemie 1886, 238, 88.
34. Tilden; Chem.News., 1892, 65, 265.
35. Weber; J.Soc.Chem.Ind., 1894, 13, 11.
36. Kondakow; Journ.Prakt.Chem., 1900, 62, 175.
37. Kondakow; Journ.Prakt.Chem., 1901, 64, 109.
38. Harries; Ann.der Chemie 1913, 383, 157.
39. Pond; J.Amer.Chem.Soc., 1912, 36, 177.
40. Harries; Ann.der Chemie 1913, 395, 211.

41. Gladstone and Hibbert; J Chem Soc., 1888, 53, 680

42. Macallum and Whitby; Trans.Roy.Soc,Can., 1924, 18, 191.

43. Scheibe and Pummerer; Ber., 1927, 60,2163.

44. Harries; Ber., 1904, 37,2708.

45. Harries; Ber., 1905, 38,1195

46. Pickles; J.Chem. Soc., 1910, 97,1086

47. Ostromisslenski; J.Russ.Phys.Chem.Soc., 1912, 44, 204.

48. Willstätter Ber., 1905, 38,1975

49. Harries;Untersuchungen über die Kautschukarten 1919,p.51.

50. Ostromisslenski:J.Russ.Phys.Chem.Soc., 1915, 47,1915.

51. Kirchhof; Oesterr,Chem.ZEit. 1922, 25,143,150

52. Boswell; Ind.Rubb.J., 1922, 64, 983.

53. Olivier; Rec.Trav.Chem. 1921, 40, 665.

54. Midgley and Henne; J.Amer.Chem.Soc., 1929, 51,1215.

55. McGavack; Ind.Eng.Chem., 1923, 15, 961.

56. Ostromisslenski; J.Russ.Phys.Chem.Soc., 1916, 48,1132.

57. Weber; Ber., 1900, 33, 779.

58. Fisher Gray and McColm;J.Amer.Chem.Soc., 1926, 48:1309.

59. Geiger; Helv.Chim.Acta. 1927, 10,530,539

60. Staudinger; Kautschuk, 1927, p.63.

61. Hinrichsen,Quensell and Kindscher; Ber., 1913, 46,1883

62. Harries;

63. Staudinger and Widmer; Helv.Chim.Acta., 1926, 9, 529.

64. Staudinger and Widmer; Helv,Chim.Acta., 1924, 7, 842.

65. Harries; Untersuchungen über die Kautschukarten, 1919, p. 48.
66. Hinrichsen; Ber., 1913, 46, 1283.
67. Wilstätter and Waldschmitz-Leitz; Ber., 1921, 54, 122.
68. Harries; Ber., 1901, 34, 2991.
69. Weber; Ber., 1902, 35, 1947.
70. Alexander; Chem. Zentr. 1904, (ii) 705.
71. Emden; Ber., 1925, 58, 2522.
72. Ditmar; Ber., 1902, 35, 1401.
73. Harries; Ber., 1902, 35, 3256.
74. Ditmar; Monatsch. 1904, 25, 464.
75. Fisher; Ind. Eng. Chem. 1927, 19, 1333.
76. Allesandri; Atti, accad. Lincei 1915, 24 (i.e) 62.
C.A. 1915, 9, 2240.
77. Bruni and Geiger; Rubber Age 1927, 22, 187.
78. Pummerer Andriessen & Gündel; Ber., 1928, 60, 1591.
79. Spence and Galletly; J. Amer. Chem. Soc., 1911, 33, 190.
80. Robertson and Mair; J. Soc. Chem. Ind., 1927, 46, 41T
81. Bruson Sebrell & Calvert; Ind. Eng. Chem., 1927, 19, 1033.
82. Hinrichsen & Kindscher; Ber., 1913, 46, 1291.
83. Kirchhof; Kolloid-Ztg., 1914, 14, 35.
84. Meyer and Mark; Ber., 1928, 61, 1939.
85. Spiller; J. Chem. Soc., 1865, 3, 44.
86. Herbst; Ber., 1906, 39, 523

87. Peachey; J.Soc.Chem.Ind., 1912, 31,1103.

88. Peachey and Leon;J.Soc.Chem.Ind., 1918, 37, 55T.

89. Kirchhof; Koll-Zeitsch. 1913, 13, 49.

90. Ostwald; J.Soc.Chem.Ind., 1913, 32, 179.

91. Boswell,Hambleton,Parker & McLaughlin,I.R.J. 1922,64 986.

92. Görter; Le caoutchouc et le gutta-percha.1915, 12,8724.

93. Bruni & Pelizzola; India Rubber J. 1922, 64, 986.

94. Whitby; India Rubber J. 1922, 63, 742.

95. Marquis & Heim; Bull.Soc.Chim. 1913, 13(4)862,

96. Kirchhof; Koll-zeitsch., 1920, 27, 311.

97. Kirchhof; Koll-Zeitsch., 1922, 30, 176.

98. Oesterle; Arch.Pharm., 230. 641-674.

99. Tschirch; Arch.Pharm., 1903,24, 481-95.

100. van Romburgh; Ber., 1904, 37,3440-3.

101. van Romburgh; Proc.K.Akad.Wetensch.Amsterdam. 1905, 8,137.

102. Caspari; J.Soc.Chem.Ind., 1902, 21,1274-78.

103. Ramsay,Chick & Collingridge; Ind., 1902, 21,1367-72

104. Tschirch & Schereschewski; Arch.Pharm.1905,243, 358-77.

105. Cohen; Arch.Pharm.1907,245, 245.

106. Dawson and Porritt;Trans,Inst.Rubb.Ind.1927, 2, 354-53.

---oOo---